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IV.—THE RELATION OF CARBON DIOXIDE TO PROTEOLYSIS IN THE RIPENING OF CHEDDAR CHEESE.

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In 1880 Babcock[1] carried on some experiments in cheese curing, in which he attempted to measure the amount of carbon dioxide formed by cheese in ripening, but his study of each cheese was limited to short periods of time and the source of the carbon dioxide formed was not ascertained by him. The investigation described in this paper was undertaken primarily to learn to what extent carbon dioxide is given off by American cheddar cheese during long periods of time in the process of ripening. It was hoped that by such study we should be able also to learn the sources of the carbon dioxide thus formed and add to our knowledge in regard to some of the deep-seated chemical changes occurring in the ripening of cheddar cheese.

As material for use in carrying on the investigation, we made two cheeses. One was normal in every respect; the other was made from milk containing chloroform and was kept under antiseptic conditions, thus enabling us to suppress factors of biological activity. The study was continued for

[1] Cornell Univ. Expt. Sta. Rept., pp. 9–27 (1879–80).

thirty-two weeks, at the end of which time we completed the work by making a study of the end-products in each cheese, including, more particularly, diamido compounds and their secondary cleavage-products and tyrosine.

EXPERIMENTAL PART.

Preparation of Cheese.

For each cheese we used about 20 kilograms of milk that had been drawn from the cows' udders not more than three hours. One cheese was made in the usual manner, being normal in every respect. In making the other cheese, we added to the milk at the start 4 per cent, by volume, of chloroform, and then enough lactic acid to equal 0.2 per cent of the milk by weight. The rest of the process of cheese-making was carried on in the usual way. In both cases salt was added at the rate of 1 part for 400 parts of milk used. The normal cheese weighed 3,000 grams. The cheese containing chloroform weighed 3,203 grams, owing to the retention of chloroform and more water.

Arrangements for Collecting Gas Evolved by Cheese.

On April 1, 1902, each cheese was placed by itself under a bell-jar, each bell-jar being connected with its own apparatus for the absorption of carbon dioxide. During the entire period of the investigation the cheeses were kept at a temperature of 15°.5 C. Through the bell-jars, made tight by mercury joints, were passed daily about 8 liters of air, previously purified by passage through several wash-bottles containing potassium hydroxide. The air from the bell-jar containing the normal cheese was passed through a drying-train of strong sulphuric acid and calcium chloride and then through two Liebig bulbs, in order to absorb any carbon dioxide present. A water-bottle holding 8.5 liters was used as an aspirator. The aspirator was started each morning at about eight o'clock and stopped at 5 P.M. Over night a stop-cock, separating the bell-jar from the wash-bottles containing potassium hydroxide and used for washing the inflowing air, was closed to prevent backward diffusion and consequent loss of carbon di-

oxide. The bulbs were weighed daily in the early period of the experiment, but only weekly during the later period.

In the case of the cheese containing chloroform, the air from the bell-jar was passed through sulphuric acid and then through silver nitrate solution, in order to absorb any hydrochloric acid formed by decomposition of chloroform. The air was then passed through three flasks containing a decinormal solution of barium hydroxide, to absorb the carbon dioxide, and finally through a potassium hydroxide guard. The same precaution against backward diffusion was observed as in the case of the other cheese. We could not employ Liebig absorption-bulbs and direct weighing, since the air coming from the bell-jar was constantly laden with vapor of chloroform. To replace the loss of chloroform caused by aspiration, fresh portions of chloroform were added, from time to time, through a separatory-funnel passing through the top of the bell-jar. A small dish placed on the top of the cheese received the chloroform. Once a week the barium carbonate formed was filtered through a weighed Gooch crucible, washed with dilute ammonia, dried, and weighed. From the amount of barium carbonate thus found the amount of carbon dioxide was calculated. On April 1st this cheese contained 12 per cent of chloroform, and on Nov. 28th, at the close of the investigation, 10.5 per cent.

The normal cheese, before being placed under the bell-jar, was completely covered on the outside by a mixture of vaseline and creosote, in order to prevent as far as possible the growth of any molds on the surface of the cheese. This was done at the suggestion of the Station bacteriologist, Mr. H. A. Harding. In a similar experiment, when no special precautions were used, Babcock[1] found it impossible to prevent the growth of molds on the surface of cheese contained in a moist atmosphere under a bell-jar. He calls attention to the fact that the growth of mold was responsible for the formation of large quantities of carbon dioxide. It was absolutely essential, therefore, that in our work we should eliminate this source of carbon dioxide, if we were to learn anything definite

[1] Cornell Univ. Expt. Sta. Rept., p. 21 (1879-80).

about other sources of carbon dioxide formation within the cheese.

Production of Carbon Dioxide in Normal Cheese.

On the first day we found the normal cheese had given off 0.044 gram of carbon dioxide, on the second day 0.0978 gram, on the third day 0.118 gram, and on the fourth day 0.139 gram. On the eleventh day, the maximum daily record up to that time was made, 0.146 gram. During the first week we found 0.735 gram of carbon dioxide, and this amount gradually decreased until the end of the fourth week, when the amount was 0.364 gram. At this time the bell-jar was opened and samples taken for chemical analysis. Before opening the bell-jar the aspiration was quickened somewhat in order to reduce the carbon dioxide in the bell-jar to the lowest amount possible. From the fourth to the ninth week the amount of carbon dioxide produced increased gradually, reaching 0.644 gram for the ninth week. At this time a small patch of blue mold, covering about a square inch of surface, was observed. This was scraped off and more creosote applied. At the end of the eleventh week another small patch of blue mold was noticed and the amount of carbon dioxide formed had again risen. Again, at the end of the thirteenth week, another small patch of mold was found, and the amount of carbon dioxide produced during this week was equal to that found during the first week of the experiment, 0.735 gram, the maximum weekly yield during the investigation. The whole outer surface of the cheese was then treated anew with the mixture of vaseline and creosote and afterwards no further trouble was experienced from the presence of molds. It was very noticeable that the presence of mold was quickly revealed by a sudden and marked increase in the amount of carbon dioxide formed. From the end of the thirteenth week to the close of the investigation, at the end of the thirty-second week, the amount of carbon dioxide gradually decreased, being only 0.224 gram during the last week.

During the entire period of thirty-two weeks the total amount of carbon dioxide produced was 15.099 grams. This

is equal to 0.5 per cent of the fresh cheese and represents a loss of solids equal to one-half pound for 100 pounds of cheese. Undoubtedly other gases or volatile compounds are formed in small quantities, as shown by the blackening of the sulphuric acid in the drying-train. We hope to make later a more detailed study of the other gases formed in cheese during the ripening process. In the table following we present the detailed results of our work week by week :

Table I.—Amount of Carbon Dioxide Formed in Normal Cheddar Cheese during Each Week of Investigation.

No. of week.	Gram of CO_2 formed.	No. of week.	Gram of CO_2 formed.	No. of week.	Gram of CO_2 formed.
1	0.735	12	0.406	23	0.462
2	0.672	13	0.735[1]	24	0.357
3	0.420	14	0.476	25	0.343
4	0.364	15	0.441	26	0.427
5	0.476	16	0.434	27	0.400
6	0.574	17	0.539	28	0.366
7	0.525	18	0.469	29	0.340
8	0.574	19	0.448	30	0.300
9	0.644[1]	20	0.497	31	0.260
10	0.539	21	0.539	32	0.224
11	0.651[1]	22	0.462		

Production of Carbon Dioxide in Cheese Containing Chloroform.

In the cheese containing chloroform we planned to suppress all biological activity. In order to ascertain how completely we succeeded in this respect, Mr. John Nicholson, the assistant bacteriologist of the Station, made bacteriological examinations from time to time. His results showed that the cheese was practically sterile throughout the entire period of the investigation.

The quantity of carbon dioxide produced by this cheese amounted only to about 0.019 gram a day during the first week, after which it fell off rapidly, the amount during the third week being less than 0.003 gram a day. At the end of three weeks carbon dioxide practically ceased to be formed. The total amount of carbon dioxide produced by this cheese was 0.205 gram, about three-fourths of which was given off during the first nine days.

[1] Increase due to presence of small amount of mold.

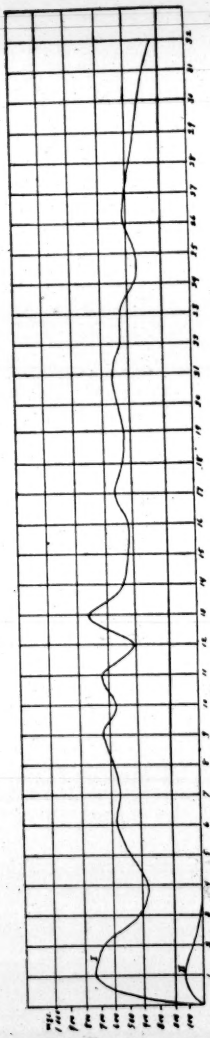


Fig. 1.

In the accompanying diagram we show in graphic form the amounts of carbon dioxide produced by the two cheeses during the period of investigation.

Proteolytic End-Products in the Normal Cheese.

At the end of thirty-two weeks the normal cheese was taken from the bell-jar, the covering of vaseline and creosote was removed, and also the entire outer rind of the cheese to the thickness of about 0.5 inch. The remainder of the cheese was cut up into small pieces and dried at 60° C. for several days. It was then broken into finer particles and again dried, after which it was extracted with ether to remove fat and then reduced to a finely powdered, white mass. This mass was extracted with several portions of water at 50° C. until about 12 liters were collected, the water-soluble content of the mass having been thoroughly extracted by this treatment. This extract was precipitated with tannin and filtered; the tannin in the filtrate was removed by lead acetate. The resulting precipitate of lead tannate was filtered and washed three times by suspension in water and refiltering. The excess of lead was removed by sulphuric acid, and the last traces by hydrogen sulphide. The filtrate was then carefully concentrated at 55° C. to about 4 liters, made acid with 5 per cent of sulphuric acid, and precipitated with phosphotungstic acid. The precipitate was washed with dilute sulphuric acid. The filtrate from the phosphotungstic acid precipitate was examined for tyrosine and the precipitate for oxyphenylethylamine and the hexon bases.

Tyrosine.—The filtrate from the precipitate by phosphotungstic acid was treated with barium oxide to remove the phosphotungstic acid and the barium hydroxide in the filtrate carefully removed by sulphuric acid. This filtrate was concentrated to a small volume. On standing, crystals separated from the solution, having much the appearance of tyrosine. These were filtered, redissolved in water, recrystallized several times from water after concentrating the solution, finally washed with alcohol, and dried over sulphuric acid *in vacuo*. A nitrogen determination by the Kjeldahl process gave the following results:

	Calculated for $C_9H_{11}NO_3$.	Found.
Tyrosine	7.68	7.73

The substance gave the color reactions that are characteristic of tyrosine, and was undoubtedly tyrosine. The separation of other monamido compounds was not attempted.

Oxyphenylethylamine.—About one-fourth of the phosphotungstic acid precipitate, obtained in the manner previously described, was decomposed by barium oxide and filtered. The excess of barium hydroxide was removed from the filtrate by means of carbon dioxide. The clear filtrate was concentrated at a low temperature and then treated with benzoyl chloride in dilute alkaline solution, according to the Schotten-Baumann method.[1] This method has been employed by Langstein[2] in the separation of oxyphenylethylamine formed by an intense peptic digestion of egg-albumin. An abundant precipitate separated, which was filtered and washed with cold water. It was then dissolved in hot alcohol and evaporated to a small bulk. On standing, an abundant crop of crystals separated from the solution, which were filtered, washed with ether, and dried over sulphuric acid *in vacuo*. This product had a melting-point of 169° C. (uncorr.), agreeing exactly with the oxyphenylethylamine obtained by Langstein. The following results were obtained by determining the nitrogen by the Kjeldahl method and the carbon and hydrogen by combustion:

	Calculated for $C_8H_9NO(C_6H_5CO)_2$.	Found.
C	76.50	76.19
H	5.54	5.44
N	4.06	4.10

This product was unquestionably oxyphenylethylamine, formed, as we shall point out later, from tyrosine with the accompaniment of carbon dioxide as a by-product.

Hexon Bases.—The remainder of the phosphotungstic acid precipitate, obtained in the manner previously described, was decomposed by barium oxide and the excess of barium hy-

[1] Ber. d. chem. Ges., 17, 2545 (1884); 19, 3218 (1886).
[2] Beit. für chem. Physiol. u. Pathol., 3, 229 (1902).

droxide was removed by careful addition of sulphuric acid. The resulting filtrate was worked for the hexon bases according to the Kossel-Kutscher method.[1]

(1) *Arginine.*—After separating histidine from the solution, which should contain only arginine and histidine, a determination was made of the nitrogen in this solution containing only arginine. The amount of arginine thus determined, equivalent to the nitrogen found, was only 0.364 gram, an amount too small to obtain in the form of crystals.

(2) *Histidine.*—This substance was separated as the dichloride, of which we obtained 0.850 gram. Analysis gave the following results:

	Calculated for $C_6H_9N_3O_2.2HCl$.	Found.
N	18.42	18.15
Cl	31.11	30.98

(3) *Lysine.*—We separated about 2 grams of lysine in the form of picrate, which gave the following results on analysis:

	Calculated for $C_6H_{14}N_2O_2.C_6H_3N_3O_7$.	Found.
N	18.66	18.80
C	38.40	38.44
H	4.53	4.56

(4) *Guanidine.*—The mother-liquor from the lysine precipitate was extracted by a mixture of alcohol and ether and then treated with gold chloride in very dilute hydrochloric acid solution, following the method of Winterstein and Thöny.[2] On standing, there soon separated from the solution a crystalline substance, behaving like a guanidine gold salt, yielding about 0.300 gram, which, on analysis, gave the following results:

	Calculated for $CH_5N_3.HCl.AuCl_3$.	Found.
Au	49.79	49.63

So small an amount of this substance was obtained that we were unable to make other determinations to establish its identity with greater certainty, but it is highly probable that the substance is guanidine.

[1] Ztschr. physiol. Chem., **31**, 165 (1900).
[2] *Ibid.*, **36**, 28 (1902).

(5) *Putrescine.*—We expected to separate the other cleavage-product of arginine, putrescine. The lysine solution had a strong odor of putrescine, and it was unquestionably present, but we failed in our efforts to isolate this base. It appears probable that the cleavage of arginine had only progressed as far as the formation of guanidine and ornithine, and that the latter compound had been decomposed only to a small extent, forming merely traces of putrescine. The fact that the cheese was of good flavor, except for a slight taste of creosote, indicates that putrescine could not have been present in considerable quantities.

Proteolytic End-Products in Cheese Containing Chloroform.

The cheese containing chloroform was, at the end of thirty-two weeks, treated, preparatory to extraction, in the manner described above in the case of the normal cheese. It was extracted with several portions of water at 50° C., until about 12 liters of extract were obtained, the mass having been completely extracted by this treatment. The water extract was treated with tannin and filtered, the tannin removed by lead acetate, and the precipitate filtered and well washed. The excess of lead was removed by sulphuric acid and the last trace by hydrogen sulphide. The filtrate was concentrated at a low temperature, never above 55° C., to a small volume. It was then precipitated by phosphotungstic acid, filtered, and well washed with dilute sulphuric acid.

Tyrosine.—After removing the phosphotungstic acid by barium oxide and then the barium hydroxide by careful treatment with sulphuric acid, the solution was concentrated to a small volume and set aside for crystallization. After standing several days, there separated from the solution a mixed crystalline and gummy mass. This precipitate was filtered, dissolved in a small volume of water, poured into cold 95 per cent alcohol, and allowed to stand several days. A crystalline precipitate formed at the bottom of the solution. The precipitate was filtered, redissolved in water, decolorized with charcoal, and filtered. On concentration, this filtrate deposited a copious crystalline precipitate, greatly resembling

tyrosine in appearance. These crystals were washed with ether and dried over sulphuric acid *in vacuo*. A determination gave 7.70 per cent of nitrogen, as compared with 7.73, calculated for tyrosine.

We were unable to find in this cheese any trace of oxyphenylethylamine.

Hexon Bases.—The phosphotungstic acid precipitate was decomposed by barium oxide, the barium hydroxide was removed from the filtrate by sulphuric acid, and then arginine and histidine were precipitated by silver sulphate in barium hydrate solution in the usual way.

(1) *Arginine.*—After the separation of histidine from arginine, a determination of nitrogen in the remaining solution indicated the presence of about 1.5 grams of arginine, which is by far the largest amount we have ever succeeded in separating from any cheddar cheese with which we have worked. The solution was evaporated, dilute nitric acid added, and then set aside for crystallization. After standing about a week, the solution had partly crystallized. These crystals were removed by filtration, washed with absolute alcohol and ether, and dried over sulphuric acid *in vacuo*. Analysis gave the following results:

	Calculated for $C_6H_{14}N_4O_2.HNO_3.\frac{1}{2}H_2O$.	Found.
N	28.45	28.32

To the mother-liquor was added silver nitrate with 2 or 3 drops of dilute nitric acid, and the solution was allowed to evaporate *in vacuo*. Crystals soon separated, and after a few days the entire mass was crystalline. The crystals were washed with alcohol and ether and dried over sulphuric acid *in vacuo*. A silver determination gave the following results:

	Calculated for $C_6H_{14}N_4O_2.AgNO_3.HNO_3$.	Found.
Ag	26.54	26.49

We believe we are justified in regarding this substance as arginine, beyond question. So far as we are able to learn, this is the first time arginine has been separated from a ripen-

ing cheese, and, in this case, we succeeded only when all biological factors had been eliminated.

(2) *Histidine.*—This base was separated as a dichloride. Analysis gave the following results:

	Calculated for $C_6H_9N_3O_2.2HCl$.	Found.
Cl	31.11	31.08
N	18.42	18.59

(3) *Lysine.*—This substance was easily separated as the picrate, and analyzed as follows:

	Calculated for $C_6H_{14}N_2O_2.C_6H_3N_3O_7$.	Found.
N	18.69	18.78
H	4.53	4.38
C	38.40	38.51

We were unable to separate guanidine from the mother-liquor of the lysine precipitate, and we believe it was not present. We were unable, also to detect any of the other possible cleavage-products of arginine. The solution containing lysine had no such odor as the corresponding solution obtained from the normal cheese and was, indeed, conspicuously free from the putrescine odor that was so characteristic of the lysine solutions obtained from normal cheese ripened at about 15°.5 C.

Analysis of Cheese.

At intervals determinations were made of the moisture, total nitrogen, water-soluble nitrogen, and nitrogen in the form of unsaturated paracasein lactate, of amido compounds, and of ammonia. The results are given in the table on the following page.

If we compare the two cheeses in question with reference to the data contained in the table on page 13, we notice:

1. In respect to the water-soluble compounds of nitrogen, the two cheeses did not greatly differ, the slight difference being in favor of the chloroformed cheese. Ordinarily, we should expect the normal cheese to form soluble nitrogen compounds with somewhat greater rapidity than the cheese containing chloroform. Two conditions that were present

Table II.—Results of Analysis of Cheeses.

	Age when analyzed.	Per cent of moisture in cheese.	Per cent of nitrogen in cheese.	Nitrogen expressed as percentage of total nitrogen in cheese, in form of			
				Water-soluble nitrogen.	Amido compounds.	Ammonia.	Paracasein monolactate.
Normal cheese	Fresh	36.53	3.54	6.78	2.52	0	58.47
	1 mo.	35.83	3.72	18.82	11.83	0.70	42.50
	3 mos.	34.84	3.92	25.50	17.86	1.78	33.42
	7 "	33.94	4.09	38.14	28.12	2.30	20.54
Cheese containing chloroform	Fresh	46.23	2.45	9.80	3.67	0	35.92
	1 mo.	45.77	2.50	20.80	11.20	0	22.40
	3 mos.	44.38	2.51	27.90	14.74	0	17.93
	8 "	44.37	2.73	40.30	23.10	0	7.33

furnish an explanation of these unexpected results. In the first place, some of the creosote used in coating the normal cheese diffused into the body of the cheese and exerted some antiseptic influence, retarding enzyme and bacterial action and giving proteolytic results lower than we commonly find in the case of normal cheese. In the second place, the chloroformed cheese contained about 10 per cent more water than the normal cheese. We have in our unpublished records numerous data which establish the fact that increase of moisture in cheese very noticeably increases the amount of water-soluble nitrogen compounds formed in a given time. At the last analysis, the chloroformed cheese was a month older than the normal cheese, and this fact also made greater the difference in the amount of water-soluble nitrogen compounds found in these analyses.

2. After the first month the amount of amido compounds formed in the normal cheese was greater than in the chloroformed cheese.

3. In the normal cheese ammonia was formed, though somewhat less in amount than under conditions entirely normal, while in the chloroformed cheese no trace of ammonia was formed.

4. We have previously[1] pointed out that the formation of water-soluble nitrogen compounds in cheese-ripening appears to take place at the expense of the paracasein monolactate (soluble in dilute solutions of sodium chloride). The figures in the preceding table furnish confirmatory evidence of this, since the paracasein monolactate diminishes at the same time the water-soluble nitrogen increases.

5. The amount of water-soluble proteolytic compounds formed in cheese cannot safely be used as the sole basis of comparison in respect to the extent of chemical changes taking place in ripening cheese. In the two cheeses investigated, the amounts of water-soluble nitrogen did not greatly differ, but an examination of the end-products of proteolysis showed changes much more complete in the case of the cheese containing the smaller amount of water-soluble nitrogen.

[1] This JOURNAL, 28, 417 (1902).

The true measure of cheese ripening must be found in the character and amount of the individual products formed rather than in the total amount of water-soluble nitrogen.

General Summary of Results.

We now bring together, in a form allowing ready comparison, the results that have been presented in detail in the foregoing pages:

In Normal Cheese.	*In Chloroformed Cheese.*
(1) Production of carbon dioxide:	
a. Total in thirty-two weeks, 15.099 grams.	*a.* Total, 0.205 gram.
b. Weekly variation from 0.735 gram in first week to 0.224 gram in thirty-second week.	*b.* Ceased entirely after three weeks.
(2) Proteolytic end-products formed:	
a. Tyrosine in small am'ts.	*a.* Tyrosine.
b. Oxyphenylethylamine.	*b.* No oxyphenylethylamine.
c. Arginine in traces.	*c.* Arginine in marked quantity.
d. Histidine.	*d.* Histidine.
e. Lysine.	*e.* Lysine.
f. Guanidine.	*f.* No guanidine.
g. Traces of putrescine.	*g.* No putrescine.
(3) Analysis of cheese.	
a. Ammonia formed.	*a.* No ammonia formed.
b. Amido compounds more abundant.	*b.* Amido compounds less abundant.

DISCUSSION OF RESULTS.

We have seen above that results varying in a most marked manner were obtained from the two cheeses used in our investigation. We will now consider some of these differences with a view to finding some satisfactory explanation of the facts presented.

The Sources of Carbon Dioxide in Cheese.

What was the source of the carbon dioxide produced in each

cheese? Why did the normal cheese produce relatively so large quantities of carbon dioxide over so long a period of time, and why did the chloroformed cheese produce so small quantities and for so brief a period?

As possible sources of carbon dioxide in cheese, we have (1) the milk used in making cheese, (2) the decomposition of milk-sugar in the formation of lactic acid, (3) the respiration of living cells present in the cheese, and (4) the chemical decomposition of compounds present in the cheese. We will consider these separately.

(1) *Milk as a Source of Carbon Dioxide in Cheese.*—According to Marshall,[1] fresh milk, before exposure to air, contains on an average about 4 per cent of free carbon dioxide by volume, and this is reduced one-half by aeration. In the amount of milk used by us in making each cheese, we should have about 0.800 gram of carbon dioxide. Some of this is, of necessity, lost in the process of cheese-making, but we could expect to retain in the cheese 0.200 to 0.300 gram of the carbon dioxide originally present in the milk.

(2) *The Decomposition of Milk-Sugar as a Source of Carbon Dioxide in Cheese.*—E. Kayser[2] has shown that certain lactic acid bacteria produce, as the result of their action on milk-sugar, not only lactic acid but also certain by-products, among which is carbon dioxide. The milk-sugar is undergoing decomposition all through the normal process of cheese-making, and the carbon dioxide thus formed becomes incorporated in the cheese curd to some extent. In our normal cheese, the milk-sugar actually present before the cheese was placed under the bell-jar amounted to 0.3 per cent of the cheese. This was changed into lactic acid with the accompanying formation of carbon dioxide in the early period of ripening, and the carbon dioxide thus formed, together with that occluded in the cheese mass, can readily account for the relatively large amount of carbon dioxide found during the first week in the normal cheese. In the case of the chloroformed cheese, a certain amount of the milk-sugar had undergone fermentation

[1] Special Bulletin No. 16, Mich. State Agr. Coll. Exp. Sta. (1902).
[2] Ann. Past., 8, 779 (1894).

before chloroform was added, as shown by a determination of the sugar in the curd the day after the cheese was made. The amount found was low compared with the amount present in perfectly fresh curd. Such fermentation would produce small amounts of carbon dioxide, which would be absorbed by the milk and pass into the cheese mass. Carbon dioxide thus enclosed in a cheese would again be given out into an atmosphere such as was present in the bell-jar, that is, one free from carbon dioxide.

(*3*) *Respiration of Living Cells Present in Cheese as a Source of Carbon Dioxide.*—It is well known that living cells give off carbon dioxide as the result of respiration processes. It is also known that in a fresh normal cheese of the cheddar type the number of micro-organisms, generally lactic acid bacteria, increases rapidly for about ten days, and then, after twenty-five days, falls very rapidly for a period of ten days to a relatively small number, as shown by Russell and Weinzirl.[1] In any case, we cannot look to the respiration processes of living cells in cheese as the source of the carbon dioxide formed after the first few weeks. As regards this possible source of carbon dioxide during the early age of a cheese, when the micro-organisms are present in enormous number, we should be justified in expecting that at this time the amount of carbon dioxide produced would be very much greater than that formed later, when the lactic acid organisms have largely disappeared, if their respiration is the source of any appreciable amount of carbon dioxide. The results secured by us with our normal cheese do not show that there was any such comparatively large amount of carbon dioxide produced at the time the lactic acid organisms were most abundant. The somewhat larger amount of carbon dioxide produced during the first two weeks is undoubtedly due mostly to the decomposition of milk-sugar and not to the respiration processes of living cells present in the cheese. In the case of our chloroformed cheese, we inhibited the activity of living organisms and this source of carbon dioxide did not, therefore, exist in the cheese.

[1] Ann. Rept. Wis. Expt. Sta., 13, 95 (1896).

(4) *Chemical Decomposition of Compounds Present in the Cheese.*—Emerson[1] has lately shown that tyrosine, through the action of the enzymes of the pancreas, can be converted into the oxyphenylethylamine with simultaneous cleavage of carbon dioxide, in accordance with the following representation of the reaction:

$$HO.C_6H_4.CH_2.CH(NH_2).COOH = HO.C_6H_4.CH_2.CH_2.(NH_2) + CO_2.$$

Langstein[2] has also shown the same reaction in the case of a long-continued peptic digestion of the coagulated portion of the blood-serum of a horse. Ellinger[3] has shown the formation of putrescine from ornithine and of cadaverine from lysine, with the splitting-off of carbon dioxide, by the action of bacterial ferments. The following equations represent these reactions:

$$CH_2(NH_2).CH_2.CH_2.CH(NH_2).COOH = CH_2(NH_2).CH_2.CH_2.CH_2(NH_2) + CO_2;$$

$$CH_2(NH_2).(CH_2)_3.CH(NH_2).COOH = CH_2(NH_2).(CH_2)_3.CH_2(NH_2) + CO_2.$$

Lawrow[4] found the same reactions taking place in an intense peptic auto-digestion of the stomach.

The work of Nencki and of Spiro[5] has demonstrated that phenylethylamine can be formed from phenylalanine with separation of carbon dioxide.

Of these different reactions furnishing carbon dioxide, we find in the normal cheese under investigation evidence that tyrosine has changed into oxyphenylethylamine and that the decomposition of arginine has resulted in the formation of its simpler products. We cannot say whether Nencki's reaction occurred, by which phenylalanine was changed into phenylethylamine, since we did not examine the cheese for these compounds. It is readily conceivable that such a change may take place, since E. Fischer[6] has shown the presence of

[1] Beit. für chem. Physiol. u. Pathol., **1**, 501 (1902).
[2] *Ibid.*, **1**, 507 (1902).
[3] Ber. d. chem. Ges., **31**, 3183 (1898).
[4] Ztschr. phys. Chem., **33**, 312 (1901).
[5] Beit. für chem. Physiol. u. Pathol., **1**, 347 (1901).
[6] Ztschr. physiol. Chem., **33**, 151 (1901).

phenylalanine among the cleavage-products of casein. There probably await discovery other similar reactions, now unknown, bearing on the formation of carbon dioxide in proteolytic changes.

It appears to us that the carbon dioxide formed after the first few weeks of ripening, in the case of the normal cheese, must have come very largely from the decomposition of some compounds present in the cheese, among which we were able to identify the change of tyrosine and arginine into derived products with simultaneous formation of carbon dioxide. In the case of the different normal cheddar cheeses that we have previously investigated, the arginine and tyrosine commence to undergo proteolytic change quite early in the ripening process.

Reviewing briefly our discussion about the sources of carbon dioxide in cheese, we believe, from the evidence furnished, that the carbon dioxide given off in the early age of the normal cheese came largely from the decomposition of milk-sugar by lactic acid organisms, while a small amount was probably due to the carbon dioxide present in the milk and to the respiration of living organisms present in the cheese. The carbon dioxide produced after the first few weeks could apparently come only from the decomposition of some compounds present in the cheese, and we were able to identify among such sources of carbon dioxide the cleavage of tyrosine and of arginine.

In the case of the chloroformed cheese, none of the carbon dioxide could have come from the respiration of living cells or the decomposition of compounds like arginine and tyrosine. The amount of carbon dioxide originally present in the milk, combined with that formed in the milk from the decomposition of milk-sugar before treatment with chloroform, was sufficient to furnish the small amount that was given off by this cheese.

Cause of Difference in Behavior of Normal Cheese and Chloroformed Cheese.

We have seen that, in the chloroformed cheese, only an in-

significant amount of carbon dioxide was present, and after three weeks practically none was found. In the normal cheese, carbon dioxide was found in relatively large quantities, and, even at the end of thirty-two weeks, more carbon dioxide was being formed in one week than the total amount produced in the other cheese. Why should there have been so marked a difference? The answer to this question involves a consideration of the causes that produce the proteolytic changes observed in the normal cheese-ripening process. The agencies sharing in this work are the following, so far as we know at present: (1) Some acid, (2) enzymes present in the milk before it is made into cheese, chief of which is galactase, (3) pepsin and pseudopepsin, added with rennet in the process of cheese-making, and (4) micro-organisms, chiefly bacteria.

In the case of our chloroformed cheese we had present, of these different agencies, acid, galactase, and rennet-pepsin. These agencies, under the conditions of our experiment, were unable to split carbon dioxide from tyrosine with the formation of oxyphenylethylamine, or change arginine into those of its products that we have commonly found in cheese ripening normally. As previously stated, this is the first instance in our knowledge in which arginine has been found in ripening cheese, and we were able to find it only because we had inhibited the action of living organisms. These facts suggest strongly that the active cause in our normal cheese that was responsible for the deep-seated proteolysis, accompanied by the production of carbon dioxide, was a biological factor.

It may be thought that our results fail to agree with those of Lawrow cited above, in which he succeeded by an autodigestion of a stomach in obtaining putrescine and cadaverine, probably with formation of carbon dioxide. It must be kept in mind, however, that in his work the conditions were favorable to a much more intense reaction, because he not only had a highly concentrated pepsin solution but he also kept the acid content of his digesting solution high, conditions that are not present in cheddar cheese.

It may be thought, again, that the activity of the enzymes,

galactase and rennet-pepsin, was checked in our one cheese by the chloroform, and that we should, under the circumstances, expect just such results as we obtained. In Bulletin No. 203 of this Station, we have furnished evidence showing that chloroform does not inhibit the action of galactase, and we shall later publish results, secured in cooperation with the bacteriological department, confirming our previous work. Lawrow's work showed that chloroform did not inhibit the activity of a concentrated solution of pepsin. In view of the evidence at hand, it appears to us quite improbable that, if chloroform has any inhibiting influence on galactase and rennet-pepsin, we should find these two enzymes, under the conditions of the experiment, able to furnish such end-products as arginine, lysine, and tyrosine, but unable to produce compounds resulting from further proteolysis, such as putrescine, guanidine, and ammonia. If chloroform interfered with the work of these enzymes, we should expect either that there would be no proteolysis or that we should find the same compounds that are formed in the absence of chloroform but in much smaller quantities. As a matter of fact, we find these enzymes quite as active in the chloroformed cheese as in the normal cheese in forming certain compounds, but they stop short in their work, appearing unable to produce the further cleavage that results in the production of carbon dioxide. This failure to furnish products beyond a certain point seems to us to depend upon other conditions than the presence of chloroform.

The only logical conclusion suggested by the results of our work appears to us to be that the enzymes, galactase and rennet-pepsin, are able to furnish such end-products as arginine, lysine, and tyrosine under the conditions existing in cheddar cheese but are not able to split these compounds into simpler ones with simultaneous formation of carbon dioxide. If this is true, then we must look to some other source as the active agency in decomposing primary into secondary cleavage-products of proteolysis with production of carbon dioxide. The only cause that can be suggested is a biological factor.

Several investigators have made a study of the gases in

cheese, especially in connection with the formation of holes in Emmenthaler cheese and the so-called "huffing" common to hard cheeses, and they have, without exception, attributed the formation of gases to micro-organisms. Thus, Baumann[1] found the gas in cheese examined by him to consist of 63 per cent of carbon dioxide. In this particular case he assigned *Bacillus diatryplicus casei* as the cause. Later von Klecki,[2] in a similar investigation, found gas produced in an inoculated milk containing 31.76 per cent of carbon dioxide and he attributed its formation to *Bacillus saccharobutyricus*. Adametz, Freudenreich, and Weigmann have assigned other organisms. Jensen[3] suggests that the gas that causes holes in cheese is mostly carbon dioxide, and that this comes from the action of lactic acid bacteria upon the nitrogen compounds of the cheese. While no one, probably, has yet solved the problem as to what specific organism or organisms are responsible for the deep-seated chemical changes occurring in cheese, the general tendency has been to look to some biological source as a prominent factor in cheese-ripening.

From the consideration of quite different data, we previously[4] arrived at the conclusion that there is a biological factor at work in normal cheese-ripening. In the results presented in this paper and also in the case of a large number of results not yet published, we always find that in a chloroformed cheese, where galactase and rennet-pepsin are the only proteolytic agents present, we never have ammonia formed, while we always find it early in normal cheese. In these cases the only difference appears to be the presence or absence of a biological agent.

What specific organism or combination of organisms may constitute this biological factor in cheese-ripening, we are not now able to say. In cooperation with the bacteriological department of this Station, we have work in progress by which we hope definitely to establish whether those deep-seated chemical changes in cheese-ripening, which cannot be attrib-

[1] Landw. Versuchssta., 42, 181 (1892).
[2] Centrbl. f. Bakteriol. u. Parasitenk., 2, 21 (1896).
[3] *Ibid.*, 4, 217 (1898).
[4] Bull. No. 203, N. Y. Agr. Expt. Sta., p. 244 (1901).

uted to galactase or rennet-pepsin, are due to lactic acid organisms or to liquefying bacteria and their enzymes, or to some combination of these.

Summary.

1. The object of the work described in this paper was to ascertain the extent to which carbon dioxide is formed in American cheddar cheese during long periods of time in the process of ripening, and also to learn the nature of the chemical changes that give rise to the production of this gas.

2. Two cheeses were used for this study. One was entirely normal, the other was made from milk containing chloroform and kept under antiseptic conditions. The investigation was continued thirty-two weeks, when a chemical study was made of the proteolytic end-products.

3. In the normal cheese, carbon dioxide was given off continuously, though in decreasing quantities after about twenty weeks, and had not ceased at the end of thirty-two weeks. The total amount thus produced was 15.099 grams, equal to 0.5 per cent of the fresh cheese. In the chloroformed cheese, the total amount of carbon dioxide produced was 0.205 gram, practically none being found after three weeks.

4. In the normal cheese the following end-products of proteolysis were found: Tyrosine, oxyphenylethylamine, arginine in traces, histidine, lysine, guanidine, putrescine in traces, and ammonia. In the chloroformed cheese were found the same compounds, excepting oxyphenylethylamine, guanidine, putrescine, and ammonia, but arginine was found in marked quantities for the first time in cheese.

5. A consideration of the possible sources of carbon dioxide in the two cheeses indicates that, in the case of the chloroformed cheese, the carbon dioxide came from that present originally in the milk and that formed in the milk from the decomposition of milk-sugar before treatment with chloroform. In the case of the normal cheese, the carbon dioxide given off in its early age came largely from the decomposition of milk-sugar by lactic acid organisms, while a small amount was probably due to the carbon dioxide present in the milk and to

the respiration of living organisms present in the cheese. The carbon dioxide produced after the first few weeks came apparently from reactions taking place in some of the amido compounds, among which we were able to identify the change of tyrosine and arginine into derived products with simultaneous formation of carbon dioxide. Deep-seated proteolysis can take place without formation of carbon dioxide, but not apparently beyond a certain line of cleavage.

6. In the chloroformed cheese, the only active proteolytic agents were lactic acid, galactase, and rennet-pepsin. Under the conditions of our experiments, these agents were able to form neither ammonia nor secondary amido compounds with production of carbon dioxide. The presence of chloroform could not account for this lack of action. These results suggest that, in the normal cheese, there must have been some agent at work not present in the chloroformed cheese, and that this extra factor was of a biological character.

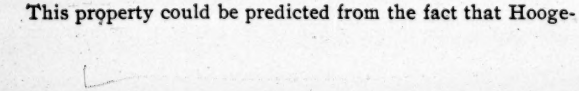
GENEVA, N. Y., February 15, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CV.—ON THE MOLECULAR REARRANGEMENT OF IMIDOACID ANHYDRIDES.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

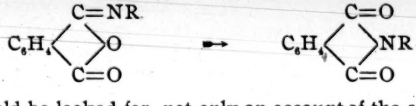
The work described in this paper was undertaken with the object of investigating the formation and properties of some imidoacid anhydrides, compounds which may be considered as substitution-products of the hypothetical monoimidoformic anhydride (I.). Derivatives of this type would be expected to undergo a molecular rearrangement into diacylamides (II.), and in the same manner substitution-products of diimidoformic anhydride (III.)should be transformed into acylamidines (IV.):



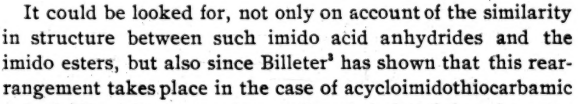
I. II. III. IV.

This property could be predicted from the fact that Hooge-

werff and Van Dorp[1] and others[2] have observed this metastatic change to take place among cyclo-compounds. For example, the isophthalimides, on heating, give phthalimides :



It could be looked for, not only on account of the similarity in structure between such imido acid anhydrides and the imido esters, but also since Billeter[3] has shown that this rearrangement takes place in the case of acycloimidothiocarbamic anhydrides. He states that α-dimethylethyldiphenylpseudodithiobiuret (V.), at 100°, is transformed smoothly into dimethylethyldiphenyldithiobiuret (VI.) :



Werner[4] found by the action of benzhydroximic chloride on silver benzoate that dibenzhydroximic acid (VII.) resulted. This oximidoacid anhydride was observed to undergo a molecular rearrangement at ordinary temperatures, giving dibenzhydroxamic acid (VIII.). In this case the benzoyl group migrates from one oxygen atom to another:

It would seem probable that, like the above, the action of anilideimide chlorides on silver salts would give imidoacid anhydrides. We therefore caused benzanilideimide chloride, in ether and in the cold, to act on dry silver acetate with the hope of obtaining the following reaction :

[1] Rec. trav. chim. Pays-Bas, **12**, 12; **13**, 93.
[2] Van der Meulen : *Ibid.*, **15**, 282.
[3] Ber. d. chem. Ges., **26**, 1688 (1893).
[4] *Ibid.*, **27**, 2198 (1894).

The product, however, did not have the above constitution. It proved to be identical with the diacylanilide prepared from mercury acetanilide[1] and benzoyl chloride. It therefore has both acyl groups attached to nitrogen, and its structure is to be represented by formula IX., the following molecular rearrangement having taken place in the cold:

IX.

When benzanilideimide chloride is allowed to act in the cold on silver parabrombenzoate a well-crystallized, stable substance is formed which, on boiling with alkali, gives a mixture of the two anilides and the two acids. To determine the structure of this substance, we allowed the imide chloride of the anilide of parabrombenzoic acid to act on silver benzoate, whereupon, instead of obtaining a different substance, it was found that the products were identical. It follows that the imidoacid anhydrides first formed in these reactions undergo a molecular rearrangement in the cold, as shown by the arrows:

$$C_6H_5C(OCOC_6H_4Br)=NC_6H_5 \rightarrowtail C_6H_5CON(C_6H_5)COC_6H_4Br \rightarrowtail BrC_6H_4C(OCOC_6H_5)=NC_6H_5.$$

As the above imidoacid anhydrides proved to be so unstable we next tried a different type of imide chloride, namely, ethylanilidochlorformate.[2] This, with silver benzoate, also gave a stable substance which, when treated with alkali, separated the benzoyl group. Since the N-diacylanilides that have been described in previous articles decompose with the liberation of the lower acyl group, it would appear that here we had to deal with a stable imidoacid anhydride. On the other hand, this conclusion was shown to be incorrect by the fact that the same substance results on treating phenylbenzimidoethyl ester with chlorcarbonic ester, a reaction involving addition which invariably gives N-derivatives.[3]

[1] Wheeler and McFarland: This JOURNAL, 18, 546 (1896).
[2] Lengfeld and Stieglitz: *Ibid.*, 16, 73.
[3] Wheeler and Walden: *Ibid.*, 19, 130; 20, 64.

$$C_6H_5N{=}C(Cl)OC_2H_5 + AgOCOC_6H_5 \rightarrow$$

$$C_6H_5N{=}C(C_6H_5)OC_2H_5 + ClCO_2C_2H_5 \rightarrow$$

$$C_6H_5N\begin{cases}COC_6H_5 + AgCl\\ CO_2C_2H_5 + C_2H_5Cl\end{cases}.$$

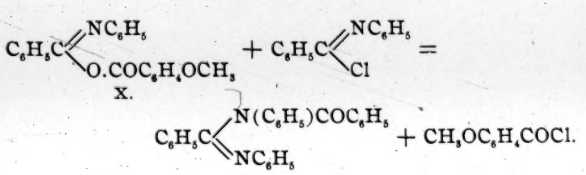
This reaction of acid chloride on the imidoester suggested that perhaps the mechanism of the action of silver salts on imide chlorides is analogous,—that the formation of N-diacylanilides does not involve a molecular rearrangement but takes place by addition. A separation of silver chloride, as indicated by the dotted lines in the following would then give the diacylanilide:

$$C_2H_5O{-}C\begin{cases}NC_6H_5\\ Cl\end{cases} + AgO.COC_6H_5 =$$

$$C_2H_5O{-}C\begin{cases}NC_6H_5.COC_6H_5\\ O\,Ag\\ Cl\end{cases}$$

That this is not the case and that imidoacid anhydrides are formed is shown by experiments with benzanilideimide chloride and silver anisate. In this case we isolated three products, the N-diacylanilide, anisic anhydride, and a compound which by a separate synthesis was identified as benzoylbenzenyldiphenylamidine. The formation of this amidine derivative and the anisic anhydride involve the previous formation of phenylimidobenzoicanisic anhydride (X.) below. Two molecules of this mixed anhydride might then decompose into anisic anhydride and a diimido anhydride, a derivative of formula III. above. This, by molecular rearrangement, would be expected to give the acylamidine.

It seems more probable, however, that the imidoacid anhydride first formed partially undergoes a molecular rearrangement, while the remainder acts with the anilideimide chloride, separating anisyl chloride and forming the amidine:



The anisyl chloride thus formed acts on a portion of the silver anisate, yielding anisic anhydride. This explanation is the more probable since Lander[1] found that benzoylbenzenyldimethylamidine results as a by-product in the action of benzmethylimide chloride on sodium ethylate, that is to say, the imide chloride acts on the imidoester first formed in the same manner as above.[2]

The results now at hand afford a satisfactory explanation for the behavior of the sodium and silver salts of amides and anilides with acid anhydrides[3] and acyl chlorides.[4] Salts of the type $C_6H_5C(NH)OAg$ give nitril and acid with acyl chlorides, while the N-substituted salts $HC(NC_6H_4)OAg$ give diacylanilides. In both cases imidoacyl anhydrides are formed as the first step of the reaction. Instead of the chloride acting by addition, as previously supposed,[5] the acyl group directly replaces the metal. The products in the former case decompose at ordinary temperatures, while those in the latter rearrange into N-derivatives. The action is similar to that of alkyl halides, but the imidoacid anhydrides undergo a molecular rearrangement with far greater ease than the imidoesters.[6]

[1] Proc. Chem. Soc. (London), **19**, 15 (1903).

[2] Lander (J. Chem. Soc., **81**, 592 (1902)) also found that benzoylbenzenyldiphenylamidine results when benzanilideimide chloride and sodium ethylate react. The reaction is simply that of an acid chloride on an imido ester (see Wheeler and Walden: *Loc. cit.*).

[3] Blacher: Ber. d. chem. Ges., **28**, 435.

[4] Wheeler and Boltwood: This JOURNAL, **18**, 381 (1896).

[5] Wheeler: *Ibid.*, **18**, 695 (1896).

[6] In regard to the molecular rearrangement of imidoesters in general, by heating with alkyl halides, the curious fact has been observed by Mr. Henry F. Merriam that the aliphatic imidoesters do not undergo this transformation under the same conditions as those found to be successful in the case of the aromatic compounds (This JOURNAL, **21**, 185; **23**, 135). For example, acetimidomethyl ester was heated with methyl iodide at various temperatures from 100° to 135°, but little, if any, molecular rearrangement took place.

The so-called new class of colored organic compounds, or imidoxanthides, which Tschugaeff[1] has prepared from benzanilideimide chloride and certain xanthogenic salts, and which are represented as being formed as follows:

$$C_6H_5C\begin{matrix}\diagup NC_6H_5\\ \diagdown Cl\end{matrix} + ROCS.SNa = C_6H_5C\begin{matrix}\diagup NC_6H_5\\ \diagdown SCSOR\end{matrix} + NaCl,$$

are probably not imido anhydrides at all but rather dithiodiacylanilides, both groups being attached to nitrogen. Thiodiacylamides, in general, are colored.

Mr. George S. Jamieson has found that the bright-red product described by Tschugaeff from benzanilideimide chloride and potassium xanthate is a stable substance. On melting it forms a varnish which, when recrystallized, gives the unaltered material melting at the same temperature. It therefore probably has the structure

$$\begin{matrix}C_6H_5CS\\ \diagdown\\ \quad NC_6H_5.\\ \diagup\\ C_2H_5O.CS\end{matrix}$$

In regard to cycloimidoacid anhydrides, it may be stated that there are three classes:

(*a*) The isoimides of Hoogewerff and van Dorp, which may be viewed as derived from the prototype, formula I., by replacing the two hydrogen atoms of the HC groups by a bivalent radical. They contain the imido group outside the ring.

(*b*) Those which are derived by replacing the hydrogen attached to nitrogen and that of the adjacent HC group, forming a ring structure. In this case an acyl group is outside of the ring, and

(*c*) Where the hydrogen attached to nitrogen and that of the more remote HC group are replaced. This class contains the entire imidoacid anhydride structure within the ring. For example, the as yet unknown oxygen anhydride of acetylanthranilic acid, XI., which should give the acetylanthranil, XII., described by Bredt and Hof,[2] belongs to this class.

[1] Ber. d. chem. Ges., **35**, 2470 (1902).

[2] *Ibid.*, **33**, 29 (1900).

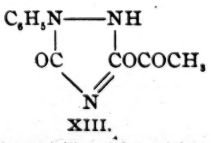
XI. XII.

Apparently no representatives of class *c*, ketometaoxazines or *β*-ketooxazolines, have been prepared. A number of cycloimidoacid anhydrides of the other class (*b*), however, are to be found in the literature.

Whether many of these compounds are actually imido anhydrides or acid amides is still an open question,[1] and, as far as the authors are aware, no member of this type of imidoacid anhydrides has been shown to undergo a molecular rearrangement.[2]

In view of the ease with which the above imidoacid anhydrides undergo a metastatic change, it seemed that this property should be met with in this series and perhaps could be used as a reliable means of distingulshing between a nitrogen and an oxygen derivative.

We selected for examination an acetyl derivative of phenylurazole. Acree[3] states that "when the silver salt of phenylurazole is treated with acetyl chloride in benzene solution in the cold, a reaction slowly takes place and the odor of acetyl chloride disappears. From the benzene solution there is obtained an oil having the constitution" XIII. (1-phenyl-3-acetylurazole):

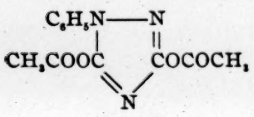


XIII.

[1] Acree has discussed the possibility of determining their structure by examining the ease with which they are saponified by boiling with alcohol and water. An anhydride should be readily hydrolyzed by boiling water. This, in some cases, may serve as an indication of an anhydride structure, but unfortunately for this test certain acylamides also liberate an acyl group by this treatment, diacetanilide for example, and it is reasonable to assume that beside acetylphthalimide many other cyclotriacylamides will be found to do the same. See Rupe and Labhardt: Ber. d. chem. Ges., **36**, 1104 (1903).

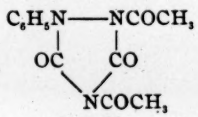
[2] A sulphur derivative of this type, *viz.*, the monobenzoyl derivative of methylaminothiopyrimidine, has been shown by Gabriel and Colman (Ber. d. chem. Ges., **32**, 2927 (1899)) to be transformed into a stable, higher melting isomer on heating.

[3] This JOURNAL, **27**, 118 (1902); Ber. d. chem. Ges., **35**, 553 (1902).



M. P. 115°.

XIV.



M. P. 162°.

XV.

When we undertook to perform this experiment we found that our results departed widely from those of Acree's. On evaporating the benzene spontaneously we obtained a beautifully crystallized mass of material and no oil. The product agreed with Acree's only in one respect—on boiling with water it reverted to phenylurazole. It therefore had the property which Acree assigns to an imidoacid anhydride. In fact, on heating to about 115° it melted, then solidified in the hot bath, and did not melt again until about 162°. The latter melting-point is that assigned by Thiele and Schleussner[1] to their diacetylphenylurazole which, on boiling with water, separates one acetyl group, giving a monoacetyl derivative melting at 170°. We found that our material, after heating, behaved in this manner and the compounds were identical. This behavior and the analytical results show that the labile compound first formed, melting at 115°, is a diacetyl and not a monoacetyl derivative. It is an imidoacid anhydride which changes into an amide derivative on heating, and the same molecular rearrangement, therefore, occurs in this series as in those previously considered.

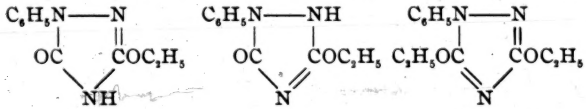
In regard to the structure of these products, it is probable that in the case of Thiele's monoacetyl derivative, not saponified by water, the acetyl group is at 2, the most basic position.

Since the labile compound, melting at 115°, gives up both acetyl groups on boiling with water, one cannot be at position 2. This leaves a choice of positions 3 and 4, 3 and 5, or 4 and 5, the latter being the least probable of all, while from the behavior of ethyl iodide with the silver salt described below the positions 3 to 5 are most probable (formula XIV.). The diacetylurazole melting at 162° is best represented by the amide structure shown by formula XV. (1-phenyl-2,4-diacetyl-

[1] Ann. Chem. (Liebig), **293**, 171.

urazole); the molecular rearrangement therefore involves a double change as shown by the arrow.

Several years ago Dr. Bayard Barnes and the writer[1] prepared an ethoxyphenylurazole, soluble in alkali, from carbethoxythionurethane and phenylhydrazine. To this substance we assigned the structure represented by formula XVI.[2]



XVI. XVII. XVIII.

In his paper on the constitution of phenylurazole Acree states that by treating the silver salt of the urazole with ethyl iodide an isomeric ethoxyphenylurazole was obtained. He states that this isomer is insoluble in alkali, and, therefore, he assigns the structure XVII. to the compound.

It seemed incredible that a monoethyl derivative of phenylurazole should be insoluble in alkali. It is the usual experience[3] that two such tautomeric formulas as XVI. and XVII. represent a single chemical individual and not two distinct substances. In our work[4] on the amidines, we encountered no case of isomerism like this.

We therefore treated the silver salt of phenylurazole with ethyl iodide in the cold, according to directions, and obtained an oil which gradually solidified, as stated by Acree. This product was a mixture of regenerated phenylurazole and a compound insoluble in alkali. The insoluble material had all of the properties which Acree assigns to the compound, except that it melted at 46° to 47° instead of at about 141°. Our analytical results showed conclusively that this material

[1] J. Am. Chem. Soc., **22**, 368 (1900).

[2] It has not been proved that this substance has not the isomeric structure, 1-phenyl-5-ethoxyurazole. The rule which has been observed in the action of phenylhydrazine on thionurethanes (This JOURNAL, **27**, 259 (1900)), would suggest, however, that formula XVI. is correct.

[3] Marckwald: Ann. Chem. (Liebig), **286**, 356 (1895); Pechmann: Ber. d. chem. Ges., **28**, 869, 2362 (1895); Dimroth: *Ibid.*, **35**, 1038 (1902); Ley and Holzweissig: *Ibid.*, **36**, 18 (1903).

[4] This JOURNAL, **19**, 367 (1897); *Ibid.*, **20**, 853 (1898); Ber. d. chem. Ges., **32**, 35 (1899).

is not a mono-, but a diethyl derivative, and the insolubility is therefore explained. Formula XVIII. represents the structure of the compound, since on boiling with hydrochloric acid it readily gives off the ethyl groups and is converted into phenylurazole. There is, therefore, no reason to select any other than the usual one of the five tautomeric forms of phenylurazole as especially representing its structure.[1]

It is interesting to note in connection with the above molecular rearrangements that the formation of nitrosoacid anilides from *syn-* and *anti*-diazo acetates[2] involves a metastatic change similar to that observed by us. The analogy is shown on comparing formulas I. and II. with the following:

The molecular rearrangement of O-acetylacetoacetic ester[3] to the C-isomer is also comparable to that which we describe.

The results of our work, so far, indicate that when an acyl derivative, stable on heating, is obtained from a compound having the structure —CONH— or —C(OH)=N— the acyl radical is attached to nitrogen.

EXPERIMENTAL PART.

Benzanilideimide Chloride and Silver p-Brombenzoate.—Eight grams of the former and 14 grams of the latter were suspended in 110 cc. of dry ether and allowed to stand at ordinary temperature. At the end of twelve hours the imide chloride had completely reacted with the silver salt and a beautiful mass of colorless prisms had separated from the ethereal solution. The material melted at 149° to 150°, without purification, and when crystallized from alcohol it melted constantly at 150°. A nitrogen determination gave:

	Calculated for $C_{20}H_{14}O_2NBr$.	Found.
N	3.68	3.37

[1] Compare Busch: Ber. d. chem. Ges., **38**, 1562 (1902). Knorr: *Ibid.*, **28**, 708 (1895).

[2] Hantzsch and Wechsler: Ann. Chem. (Liebig), **325**, 229 (1902).

[3] Claisen and Haase: Ber. d. chem. Ges., **33**, 3778 (1900); Wislicenus and Körber: *Ibid.*, **34**, 218 (1901).

p-Brombenzanilideimide Chloride, $BrC_6H_4C(Cl)=NC_6H_5$.—Parabrombenzoic anilide (15.3 grams) and phosphorus pentachloride (13.5 grams) were heated to 150° to 160° and the phosphorus oxychloride distilled off as far as possible at this temperature. On cooling, a mass of long needles separated which, on washing with ligroin, melted at about 78°. This imide chloride was found to be very sensitive towards moisture. On attempting to crystallize the material from ligroin it reverted to the anilide. The material for use was distilled at 12 mm. pressure, whereupon it practically all boiled at 200° to 210°, mostly at 205° to 207°. A portion of this, which melted at 78°, was analyzed with the following result:

	Calculated for $C_{13}H_9NClBr$.	Found.
N	4.75	4.87

This imide chloride is easily soluble in benzene and ligroin.

p-Brombenzanilideimide Chloride and Silver Benzoate.—The freshly distilled imide chloride (5.7 grams) was dissolved in dry benzene and the silver benzoate (6 grams) added. In this case the mixture was warmed for about one hour on the steam-bath. After filtering and cooling, the benzene deposited minute crystals which, when crystallized from alcohol, formed beautiful long needles or prisms. These melted at 150° and when they were mixed with some of the material prepared in the opposite way the melting-point was not lowered. A nitrogen determination gave:

	Calculated for $C_{20}H_{14}O_2NBr$.	Found.
N	3.68	3.83

p-Brombenzoylbenzanilide, obtained by these methods, is readily soluble in hot alcohol, but difficultly in cold, and more easily in benzene. When warmed with alkali, in alcoholic solution, it gives a mixture of parabrombenzanilide, benzanilide, benzoic, and parabrombenzoic acids.

Benzanilideimide chloride and silver acetate reacted slowly in cold ether. At the end of twelve hours the reaction was complete. On evaporating the ethereal solution in a vacuum the crude crystalline residue, washed with water, melted at about

62° to 63°. On crystallizing from dilute alcohol it melted at 68° and proved to be identical with acetbenzanilide previously described.[1]

Ethyl Phenylimidochlorformate and Silver Benzoate.—Five grams of the ester and 7 grams of the salt were mixed in dry ether and allowed to stand. At the end of twelve hours the ether still contained a large amount of chloride, and a strong odor of phenylisocyanate was noticeable. The mixture was then heated for three hours on the water-bath, when it was filtered and the ether evaporated spontaneously. A beautiful mass of prisms separated, which melted at about 65°. When crystallized from alcohol it formed colorless prisms and melted at 67° to 68°. A nitrogen determination gave:

	Calculated for $C_{16}H_{15}O_3N$.	Found.
N	5.20	5.38

Phenylimidoethyl benzoate and ethyl chlorcarbonate did not react at ordinary temperatures and no action was observed when the mixture was boiled. Finally a reaction took place on heating in a closed tube at 120° to 140° for six hours. When the tube was opened, ethyl chloride was evolved and an oil was obtained which deposited a solid on stirring with ether. This material formed prisms from alcohol, melted at 67°, and proved to be identical with that obtained in the above experiment. The substance is, therefore, benzoylphenylurethane, $C_6H_5N(COC_6H_5)CO_2C_2H_5$. When this is warmed with alcoholic sodium hydroxide, benzoic acid, and phenylurethane are obtained.

Benzanilideimide Chloride and Silver Anisate.—Four grams of benzanilideimide chloride and 5.1 grams of silver anisate were suspended in dry ether and allowed to stand for sixteen hours, when the ethereal solution gave no test for imide chloride. The ethereal solution was then filtered and spontaneously evaporated, whereupon a mass of long, slender, colorless

[1] Wheeler and McFarland: This JOURNAL, 18, 546 (1896). A sample of pure, dry formylbenzanilide, which originally melted at 112° and was a portion of the analyzed material, on keeping in a specimen-tube for seven years, was found to have decomposed quantitatively into benzanilide. The original prismatic shape of the crystals was retained, but they had become opaque and melted sharply at 162°.

prisms, mixed with some plates, was obtained. The mixture was washed with alcohol and the prisms crystallized from alcohol. They melted at 97° to 98°, were free from nitrogen, and on boiling with dilute alcoholic hydrochloric acid gave anisic acid. This material is therefore anisic anhydride, which is said to melt at 99°.[1]

When water was added to the alcoholic washings from the above, tables separated. These melted at 162° to 163°, after crystallizing several times from alcohol. This material was shown to be benzoylanisanilide by preparing the same substance from

Phenylimidoethyl Benzoate and Anisyl Chloride.—The anilide was obtained very smoothly by heating the mixture at 110° to 120° for six to seven hours. It was very soluble in alcohol and benzene and was purified by crystallizing from alcohol, from which it separated in six-sided tables and melted at 162° to 163°. When mixed with the above preparation the melting-point was not lowered. A nitrogen determination gave:

	Calculated for $C_{21}H_{17}O_3N$.	Found.
N	4.22	4.55

In another experiment the mixture of benzanilideimide chloride and silver anisate was boiled in ether for two and a half hours, when the reaction was complete. On evaporating the ether the residue consisted of prisms of anisic anhydride and a considerable amount of lozenge-shaped crystals. By fractional crystallization from alcohol a separation was effected and a compound melting at 171° was isolated. That this was not anisic anilide (also melting at 171°) was shown on mixing, whereupon the mixture melted at 148° to 155°. When mixed with the diacyl anilide, melting at 162° to 163°, it melted below 155°. A nitrogen determination agreed with the calculated for benzoylbenzenyldiphenylamidine:

	Calculated for $C_{26}H_{20}ON_2$.	Found.
N	7.4	7.7

Benzoylbenzenyldiphenylamidine was prepared for compari-

[1] Pisani: Ann. Chem. (Liebig), **102**, 284.

son by treating the amidine with benzoyl chloride. The product crystallized beautifully from alcohol, in the characteristic lozenge-shaped crystals, and melted at 171°. When mixed with the above the melting-point was not altered. This substance has recently been described by Lander.[1] He gives the melting-point at 170° to 172°.

Anisanilideimide Chloride, $CH_3OC_6H_4C(Cl)=NC_6H_5$, was prepared in the usual manner. It could not be distilled under diminished pressure without almost complete decomposition. A portion which distilled at 220° to 230° at 17 mm. pressure solidified on cooling, and when crystallized from petroleum ether formed colorless prisms, melting at 70°. With water it was converted into anisanilide, melting at 171,° which is said to melt at 168° to 169°.[2] A nitrogen determination gave:

	Calculated for $C_{14}H_{12}ONCl$.	Found.
N	5.7	6.0

Benzanilideimide chloride and silver m-nitrobenzoate in ether reacted with the greatest ease. In one hour the action was complete and a beautiful mass of colorless prisms had separated from the ethereal solution. Without purification they melted at 136°, and when crystallized from alcohol the melting-point did not rise beyond 139°. The compound was melted and recrystallized without altering the melting-point. When warmed with alkali, benzanilide was obtained. A nitrogen determination agreed with the calculated for *m*-nitrobenzoylbenzanilide, $C_6H_5CONC_6H_5.COC_6H_4NO_2$:

	Calculated for $C_{20}H_{14}O_4N_2$.	Found.
N	8.09	8.37

Labile Diacetylphenylurazole.—The silver salt of phenylurazole was prepared by Acree's directions and allowed to stand with one molecular proportion of acetyl chloride in cold dry benzene for three days. Heat was evolved when the silver salt and acid chloride were brought together. On spontaneously evaporating the benzene a beautiful mass of colorless

[1] *Loc. cit.*

[2] Lossen: Ann. Chem. (Liebig), 175, 292: Leuckart: J. prakt. Chem., 41, 312.

prisms was obtained which, when rapidly heated, melted quite sharply at 113° to 115°. At about 120° the melted mass solidified again and did not melt completely until about 162°. This labile product was very soluble in benzene. On warming in this solvent and then precipitating with petroleum ether, material melting less sharply was obtained. A nitrogen determination was therefore made, using the original sample :

	Calculated for $C_{10}H_9O_3N_3$.	Calculated for $C_{12}H_{11}O_4N_3$.	Found.
N	19.17	16.09	16.10

When this material was allowed to digest on the steam-bath in dilute alcohol it was converted into phenylurazole.

Stable Diacetylphenylurazole.—Some of the labile product was heated in an oil-bath at 120° to 140° for a short time. It melted and solidified again in the hot bath. On crystallizing then from alcohol it melted at 162°. This material proved to be identical with the diacetyl derivative described by Thiele, which we obtained according to his directions by heating the urazole with acetic anhydride. When the products were mixed the melting-point was not lowered. It was found that Thiele's diacetyl derivative could be crystallized from alcohol. A nitrogen determination, in the case of our material melting at 162°, gave :

	Calculated for $C_{12}H_{11}O_4N_3$.	Found.
N	16.09	16.5

When this diacetyl derivative was boiled with water it was converted into the monoacetyl derivative described by Thiele, which melted at 170°.

1-Phenyl-3,5-diethylurazole.—Eleven grams of silver phenylurazole and 6 grams of ethyl iodide were mixed in benzene and allowed to stand for thirty hours. The salt then appeared to be largely unaltered. Six grams more ethyl iodide were added and the mixture let stand for forty-eight hours longer. It was then filtered and the benzene was evaporated on the steam-bath. By boiling the silver residue with alcohol, phenylurazole was obtained. The amount represented

about one-quarter of the urazole originally combined as silver salt. After evaporating the benzene an oil was obtained which finally solidified. This solid showed no definite melting-point. On treating the solid with cold ether the greater portion dissolved, leaving behind some phenylurazole. The ether extract was shaken thoroughly with alkali and washed, and then evaporated to dryness. The oil obtained soon solidified. The solidification took place by radiation from various points through the oil until the whole solidified to a botryoidal crystalline mass. When this cake, melting at 45° to 47°, was crystallized from ligroin it formed colorless needles which melted at 46° to 47°. Nitrogen determinations gave:

	Calculated for $C_{10}H_{12}O_2N_2$.	Calculated for $C_{12}H_{16}O_2N_2$.	Found. I.	Found. II.
N	20.59	18.02	17.85	18.07

The diethyl derivative insoluble in alkali and phenylurazole were the only products that we obtained in this reaction. The supposed mono-derivative of Acree was possibly a mixture of about equal parts of these compounds. Such a mixture would give results, on analysis, agreeing with those for a monoethyl derivative.

An analysis of the white silver salt used in the above experiment gave 39 per cent silver, while the calculated for a monosilver salt is 37.9 per cent. It is, in all probability, a monosilver salt. The fact that it gives a diacetyl and a diethyl derivative is a very curious result. In all probability a portion of the salt reacts with ethyl iodide on another portion in a manner similar to that observed by Lander[1] in the case of the action of silver oxide and alkyl halides on acid amides. It effects alkylation by combining with hydrogen iodide, which otherwise would be set free.

NEW HAVEN, CONN., February, 1903.

[1] J. Chem. Soc. (London), **79**, 698 (1901); **81**, 591 (1902).

THE ACTION OF OZONE, HYDROGEN PEROXIDE, ETC., ON CARBON MONOXIDE.

By Wm. App Jones.

In 1876 Remsen and Southworth[1] found that carbon monoxide is not oxidized by ozone, even when it is mixed with ozonized oxygen and placed in direct sunlight. The ozonizer used was of the form described by Wright.[2]

Baumann[3] showed that carbon monoxide is oxidized by the action of palladium hydrogen and oxygen.

Keiser,[4] repeating some unpublished work by Broun, found that there is no action upon carbon monoxide at the temperature at which the ozone is broken down by heat. No carbon dioxide is formed when the monoxide is passed through hydrogen peroxide which is being rapidly decomposed by heat. Leeds[5] and Baumann[6] state that the monoxide is oxidized by air and moist phosphorus. Keiser repeated this experiment but found no oxidation. There was a precipitation of barium carbonate in the baryta water, but this was shown to come from carbon in the phosphorus. No phosphorus compounds were found mixed with the barium carbonate.

In the course of his work Keiser confirmed the work of Traube,[7] who showed that carbon monoxide is changed to dioxide under the influence of palladium and hydrogen peroxide.

Theoretically, carbon monoxide is an unsaturated compound, and as such should readily combine with other substances. It unites directly with chlorine, and we would expect it to combine with oxygen without difficulty. The experiments briefly outlined above seem, on the whole, to show that such is not the case, but as there was still room for doubt it was suggested by Professor Remsen that the work be repeated, taking even greater precautions than ever before.

[1] Remsen and Southworth: Am. J. Sci., [3], 11, 136 (1876); Ber. d. chem. Ges., 8, 1415.

[2] Wright: Am. J. Sci., [3], 4, 26 (1872).

[3] Baumann: Ztschr. physiol. Chem., 5, 244.

[4] This Journal, 4, 50, 454 (1882).

[5] Leeds: J. Am. Chem. Soc., 1, 232.

[6] Baumann: Ztschr. physiol. Chem., 5, 250.

[7] Traube: Ber. d. chem. Ges., 15, 2854; 16, 123.

The Action of Air and Carbon Monoxide on Moist Phosphorus.

These experiments were undertaken in order to see whether any carbon dioxide is formed by the passage of air and carbon monoxide over moist phosphorus. The apparatus used had no cork or rubber joints and contained no mercury, unlike the forms that had been used by previous workers. It consisted of a row of wash-bottles connected by fusing together their tubes.

At the very outset a serious difficulty was met with. No matter what the rate of flow of the air through the system of wash-bottles arranged thus, (1) KOH, (2) $Ba(OH)_2$, (3) P, (4) $Ba(OH)_2$, (5) KOH, although absolutely no precipitate appeared in 2, a decided deposit soon formed in bottle 4. By the time 8 or 10 liters of air had been passed, a precipitate 5 or 6 mm. deep had formed in the latter bottle.

It was soon found that when fresh phosphorus was introduced into 3, a very much larger precipitate was formed than when the air had been passed for about a day, and all the outside of the phosphorus had been burned off. Under these circumstances the precipitate in 4 was slight, but decided, and had a much more crystalline appearance than that of barium carbonate. It was at once suspected that some volatile compound of phosphorus had passed over, and this was found to be the case on testing the precipitate with ammonium molybdate. This same phenomenon was observed by Baumann,[1] but was not noted by Keiser.[2] In our case it was found necessary to introduce at least three wash-bottles, each containing about 10 cc. of pure water, between the bottle containing phosphorus and the one with the barium hydroxide. To show this we need only give the results of one experiment. After about 75 liters of air had been passed over the phosphorus and through a system of 4 wash-bottles, the contents of the latter were carefully transferred to beakers, treated with pure nitric acid, and warmed on a sand-bath in order to oxidize any phosphorus compound that might be present. The liquid was allowed to cool almost to the room tempera-

[1] Ztschr. physiol. Chem., 5, 250.

[2] This JOURNAL, 4, 454.

ture, and was then treated with a solution of ammonium molybdate in nitric acid, and the ammonium phosphomolybdate titrated according to the method of Kilgore.[1] The following results were obtained. The bottles are numbered in order after the one containing the phosphorus:

Bottle 1 required 8.7 cc. of N/7 alkali.
" 2 " 3.3 " " " "
" 3 " 0.6 " " " "
" 4 " 0.0 " " " "

These results show conclusively that some compound of phosphorus is carried over, and that several wash-bottles are required to remove it completely.

The apparatus finally used consisted of a series of wash-bottles fused together, and arranged as follows:

(1) KOH; (2) $Ba(OH)_2$; (3) P; (4) H_2O; (5) H_2O; (6) H_2O; (7) $Ba(OH)_2$; (8) KOH.

About 25 or 30 grams of phosphorus were placed in 3, which contained about 10 cc. of water through which the gas passed in order to become thoroughly saturated immediately before coming in contact with the phosphorus. When new phosphorus was introduced air free from carbon dioxide was passed over it for a day to burn off the surface. This precaution was found to be absolutely necessary. A few of the results obtained are given:

1. Ten liters of air free from carbon dioxide were passed and found to give no precipitate in bottles 2 or 7. Then 6 liters of air containing approximately 3 liters of oxygen, 0.75 liter of carbon monoxide, and 4.25 liters of nitrogen were passed through. Time, six hours. The precipitate in 7 was rapidly filtered and washed, and then dissolved in dilute hydrochloric acid, and precipitated as barium sulphate. Found, 0.1664 gram $BaSO_4$, equivalent to 0.1406 gram $BaCO_3$, or 0.03143 gram CO_2. Three-fourths of a liter of carbon monoxide should yield 1.474 gram of carbon dioxide. Hence, the amount found is 2.13 per cent of the theoretical.

2. Air used, 9 liters; carbon monoxide, 2.75 liters. Time,

[1] J. Am. Chem. Soc., **16**, 765; **17**, 950.

twelve hours. In this case the weight of barium carbonate found was 0.1872 gram, corresponding to 0.03533 gram carbon dioxide, or 0.653 per cent of oxidation.

3. The barium carbonate was decomposed by dilute hydrochloric acid and the carbon dioxide liberated was absorbed in a weighed potash-bulb. Air used, 5 liters; carbon monoxide, 0.75 liter. The weight of carbon dioxide formed was 0.031 gram, corresponding to 2.102 per cent oxidation.

It will be noticed that, under the same conditions, the results are the same, practically, and, as Baumann pointed out, the amount of oxidation varies with the amount of phosphorus exposed and the rapidity of the current.

These experiments were tried repeatedly, but always with the same result. After 10 or 20 liters of air had been passed through the system and not the least trace of a precipitate had formed in the baryta bottle used as a test, a mixture of carbon monoxide and air was then passed through, all other conditions being the same. In no instance did a precipitate fail to appear in the baryta bottle after 2 or 3 liters of the mixture had been passed through. Further, every kind of change was made in the rate of flow, and the gases were mixed in the proportions given by Keiser,[1] and also by Baumann.[2] In every case there was evidence of oxidation.

The carbon monoxide was made from potassium ferrocyanide and also from formic acid.

Baumann,[3] in one experiment, introduced the carbon monoxide beyond the bottle containing the phosphorus. This experiment was repeated, the carbon monoxide being introduced between bottles 4 and 5. There was not the least trace of oxidation, thus confirming the result of Baumann. The odor of ozone was, however, distinctly perceptible at the end of the system of wash-bottles.

Hydrogen peroxide was also placed in 5, the monoxide being introduced between 4 and 5. Here, again, there was no evidence of oxidation.

[1] Keiser: This JOURNAL, **5**, 454.
[2] Baumann: Ber. d. chem. Ges., **16**, 2146.
[3] Baumann: Ztschr. phys. Chem., **5**, 250.

The Action of Carbon Monoxide on Phosphorus in Hydrogen Peroxide.

The hydrogen peroxide was prepared by the method of Thomsen.[1] The solution was titrated with potassium permanganate and found to contain 2.424 per cent of hydrogen peroxide. The apparatus used is that described above. About 20 or 25 cc. of the pure peroxide was introduced into bottle 3, which contained 25 grams of phosphorus, the outside of which had been burned off. Before the potash bottle 1 was placed a series of wash-bottles containing an alkaline solution of pyrogallol, and the carbon monoxide used was collected in a gasometer over a similar solution. When the entire system had been filled with pure carbon monoxide, the solution of baryta water was introduced into bottle 7 and the experiment begun.

When the hydrogen peroxide and phosphorus came in contact there was not the least disturbance, and the occasional appearance of a bubble of gas on the phosphorus was the only indication of chemical action. The passage of pure carbon monoxide, about 0.75 to 1 liter per hour, was continued for thirty-six hours, and only a slight coating was observed on the inlet-tube, and no precipitate at all. This makes it appear extremely improbable that the oxidation of carbon monoxide by air and moist phosphorus is due to the action of the phosphorus on hydrogen peroxide, formed in the course of the experiment by the action of moist air on phosphorus.

When a strip of platinum was introduced into the bottle containing the phosphorus, there was, of course, oxidation of the carbon monoxide, and a quite rapid decomposition of the peroxide. This was pointed out by Traube.[2]

Repetition of the Work of Remsen and Keiser.

The work of Remsen and Keiser[3] was repeated according to the directions given by them, except that the wash-bottles were fused together instead of having ground-glass connections, and between the vessel containing the phosphorus over

[1] Thomsen: Ber. d. chem. Ges., 7, 73.
[2] Traube: Ber. d. chem. Ges., 15, 2325, 2854.
[3] Remsen and Keiser: This JOURNAL, 5, 454.

mercury and the last baryta bottle, three wash-bottles, each containing about 10 cc. of pure water, were introduced. As mentioned before, this was necessary in order to prevent some phosphorus compound from reaching the baryta bottle. It was also found necessary, whenever a new piece of phosphorus was used, to pass a current of air about a day to burn off the surface, for otherwise a large precipitate soon appeared in the baryta bottle. When these precautions were taken, 30 liters of air could be passed through the system without the least appearance of a precipitate in the test-bottle.

One experiment is here described as performed: Eighteen liters, of air, free from carbon dioxide, were passed through the apparatus, the flow being so regulated that 2 or 3 bubbles passed per second. After the passage of this amount of air, absolutely no precipitate was to be seen in the test-baryta bottle, and only a very slight coating on the inlet-tube of the bottle. Without disturbing the apparatus, a mixture of carbon monoxide and air—2 liters of the monoxide to 22 liters of air—was passed through. After the passage of 5 or 6 liters of the mixture a decided precipitate had appeared in the test-baryta bottle, and when 12 liters had passed the precipitate was about 3 mm. deep and the inlet-tube became stopped up so as to prevent the flow of the gas.

Mixtures of air and carbon monoxide in various proportions were used, and the mixture was allowed to pass at different rates, but in all cases decided precipitates appeared in the test-bottle. In no case did the air, free from carbon dioxide, cause a precipitate.

Action of Ozone on Carbon Monoxide.

In view of the quite inexplicable statements that ozone does not oxidize carbon monoxide, either at the ordinary temperature or at 300° C., it was thought that possibly ozone more concentrated than that hitherto used might be able to cause oxidation.

The ozonizer used was of the Berthelot pattern, the air-space being about 30 cm. long, the outer and inner tubes being about 3 mm. apart. The diameter of the outer tube was 3

cm. The gas entered at the top of the outer tube and escaped from the bottom. The inner tube was filled with water slightly acidulated with sulphuric acid. The entire ozonizer was placed in a cylinder containing ice-cold, acidulated water. These two solutions were the electrodes. The strongest current used was from 12 bichromate cells arranged in series, the total voltage being about 18. The apparatus was arranged as shown in the figure on the opposite page.

A Ruhmkorff coil capable of giving a spark about 16 cm. long was used.

In making blank experiments with the oxygen the stopcock O was turned so that the carbon monoxide was excluded. The wash-bottle E prevented the entrance of air, and at all times kept the carbon monoxide from diffusing back into the ozonizer.

In most of the experiments quite a rapid current of oxygen was used in order to avoid the destruction of the ozone already formed.

Using all 12 cells and passing a current of 2 liters of air per hour, the ozone was passed directly into a solution of potassium iodide, and the liberated iodine was then titrated with a standard solution of sodium thiosulphate. As determined in this way, even with such a rapid current of oxygen, 3.78 per cent of ozone was formed. This ozone had an almost insufferable odor as it came from the apparatus, and a little of it, when inhaled, produced an irritation of the throat similar to that caused by chlorine. If conducted through a rubber tube it would eat through the rubber in a few minutes.

The results are as follows: Using 12 or even 6 cells connected with the coil, the carbon monoxide was oxidized at the ordinary temperature, and still more at 250° C. Using 2 cells, there was no oxidation at the ordinary temperature, but carbon dioxide was produced at 250°. Of course, thorough blank tests were made. The ozonized oxygen, when passed through the apparatus at the ordinary temperature or at 250° to 300°, did not produce a precipitate. The same was true of the carbon monoxide at the same temperatures. There can, therefore, be no doubt that the precipitation of barium carbonate,

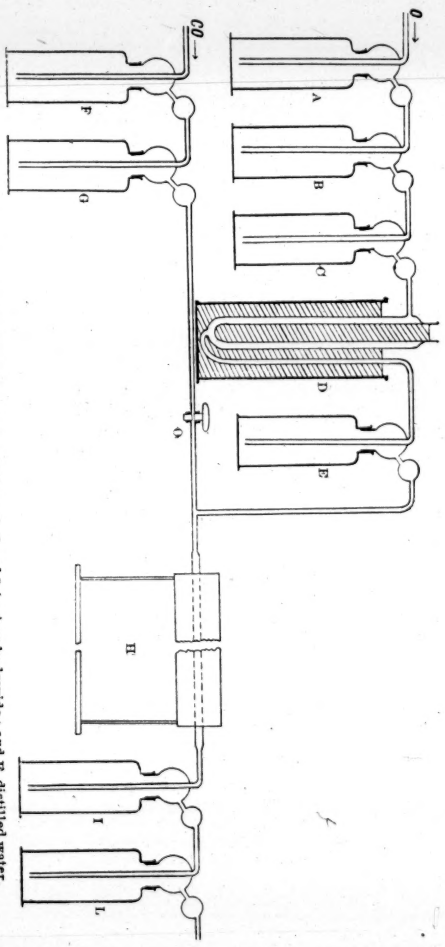


Fig. II.—Bottles A, B, F and I, contained caustic potash solution; C, G and I, barium hydroxide; and E, distilled water.

which was carefully identified, was due to the action of the ozone on the carbon monoxide.

The action of the ozone formed by the oxidation of moist phosphorus was next tried at higher temperatures. Baumann[1] showed that it does not act on carbon monoxide at the ordinary temperature, a result confirmed by our work. Accordingly, about 30 or 40 grams of phosphorus were placed in the wash-bottle C, and the outside was carefully burned off. Then baryta water was introduced into the test-bottle. The ozone formed no precipitate. Then carbon monoxide was allowed to enter by opening the stop-cock O. After the passage of 12 liters of this mixture no precipitate appeared in the bottle containing baryta water. The temperature was then raised to 250° C. After the passage of about 2 liters, a precipitate began to form and increased slowly as the current of gas was continued. These experiments were repeated a number of times, always with the same result—a slight but distinct oxidation at 250°.

The oxidizing power of ozone varies with the temperature and the concentration.

The amount of ozone formed by the phosphorus when 2 liters were passed per hour was determined by passing it through a solution of potassium iodide, and titrating the iodine with standard thiosulphate solution. The percentage of ozone was found to be 0.0021, the ozonizer giving 3.78 per cent. These results show how little ozone is formed by the oxidation of moist phosphorus. The amount of ozone cannot be estimated by the odor, for the slightest trace of it will be quite perceptible.

The Action of Strong Hydrogen Peroxide on Carbon Monoxide.

Remsen[2] has shown that ordinary hydrogen peroxide does not oxidize carbon monoxide. This work was repeated, and it was found that a solution containing 2.424 per cent of hydrogen peroxide did not cause any oxidation. But since it was found that the oxidizing power of ozone depends on the

[1] Baumann: Ztschr. phys. Chem., **5**, 250.
[2] Remsen: This JOURNAL, **4**, 50.

concentration, it seemed advisable to prepare a much stronger solution of hydrogen peroxide, and to test its action.

The pure dilute solution of hydrogen peroxide was prepared according to the method of Thomsen,[1] and was then concentrated by the method of Wolffenstein.[2]

Three specimens of hydrogen peroxide of 53, 57, and 63 per cent strength, respectively, were prepared. No difficulties were encountered in obtaining the material, but precautions were taken in case an explosion should occur.

In the experiments a series of wash-bottles, with fused connections, was used. They were arranged in the following order:

(1) KOH; (2) $Ba(OH)_2$; (3) H_2O_2; (4) $Ba(OH)_2$; (5) KOH.

In each case the hydrogen peroxide was introduced into 3 and tested for several hours by passing a stream of air free from carbon dioxide in order to see that the material caused no precipitate in the test-baryta bottle 4. Then a current of pure carbon monoxide was passed. In no case was there the least evidence of oxidation of the monoxide.

The Action of Electrolytic Oxygen on Carbon Monoxide.

Since both Traube and Richarz have shown that some hydrogen peroxide and ozone are formed during the electrolysis of acidulated water, these experiments could give no evidence, unless negative in character,—if oxidation occurred it would not prove that electrolytic oxygen caused the oxidation, for platinum and hydrogen peroxide can act in the same way under the same circumstances. However, if no oxidation took place, it would show that electrolytic oxygen has not the power to oxidize carbon monoxide. This was found to be the case. For the electrolysis, a small U-tube holding only about 15 or 20 cc. was used, the object being to have very little water present to absorb the carbon dioxide that might be formed. The apparatus was arranged as follows:

(1) KOH → (2) $Ba(OH)_2$ →
(3) KOH → (4) $Ba(OH)_2$ → U-tube → (5) $Ba(OH)_2$ → (6) KOH.

[1] Thomsen: Ber. d. chem. Ges., **7**, 73.

[2] Wolffenstein: *Ibid.*, **27**, 3307. See also Spring: Ztschr. anorg. Chem., **8**, 424; Brühl: Ber. d. chem. Ges., **28**, 2847.

In making blank tests, air was passed through bottles 1 and 2 and into the U-tube, the inlet tube being curved and projecting down into the tube so that the gas might bubble directly against the electrode C, from which the oxygen was coming off. The wire connected with this electrode passed through a T-tube inserted in the stopper, and the gas left the U-tube through the side tube E. The negative electrode B, was connected in the same way, the hydrogen going out through the side tube D, and into a vessel containing a little alkali. Where the wire entered the T-tubes the top of the tube was tightly closed with melted paraffin so that there was no communication with the outer air, thus avoiding the absorption of carbon dioxide. In no case was there any evidence of oxidation of the carbon monoxide. When this gas was bubbled directly against the electrode C, from which large quantities of oxygen were being given off, there was not the slightest precipitate formed after twelve to fifteen hours.

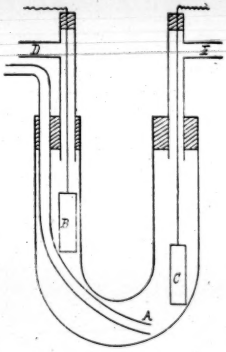


Fig. H.

JOHNS HOPKINS UNIVERSITY,
CHEMICAL LABORATORY, 1898.

THE ACTION OF OZONE ON CARBON MONOXIDE.

BY C. E. WATERS.

Because the results of Jones, which are given in the preceding article, are at variance with what had been previously stated in regard to the action of ozone on carbon monoxide, it was suggested by Prof. Remsen that the work be repeated, using a Holtz machine instead of the induction coil used by Jones. The same ozonizer was made use of, and the apparatus was arranged exactly as Jones had it, except that a wash-bottle containing sulphuric acid was placed just before the ozonizer, and the carbon monoxide was similarly dried before

passing into the heated tube H. The Holtz machine was an instrument capable of giving very powerful discharges, and was run by means of an electric motor. It soon became evident that the condition of the weather had much to do with the results. On clear, dry days the speed of the motor had to be greatly reduced, and even then there was much leakage, in spite of the wires leading to the ozonizer being enclosed in glass tubes, and sparks frequently jumped around from the inner tube to the acidulated water in the outer cylinder. Under these conditions a precipitate was always formed in the bottle containing the barium hydroxide solution. During unfavorable weather the amount of oxidation was very slight. With the induction coil no such difficulty was met with, and Jones apparently obtained equally good ozone at all times. The form of ozonizer used was found to be much more efficient than the one previously used in some of this work.[1]

Some of our results are given below. Careful blank experiments were, of course, made, and in no case was there any evidence of oxidation. There was also no formation of carbon dioxide when the ozonized oxygen and the carbon monoxide were mixed at the ordinary temperature.

Experiment 1.—One liter of carbon monoxide and 3 liters of oxygen were used, the gases being mixed, after the oxygen was ozonized, in the tube H (see page 47). Temperature, 242°. There was a slight precipitate formed in I. In this experiment a Wright ozonizer was used.

Experiment 2.—Same arrangement as in 1. Temperature 269° to 272°. Two liters of carbon monoxide and 5 liters of oxygen. Time, three and a half hours. Only a very slight precipitate was formed.

Experiment 3.—The ozonizer used by Jones was substituted in this case, the rest of the apparatus remaining the same. Temperature, 278° to 282°. Three liters of carbon monoxide and 8 liters of oxygen. Time, four hours. At first there was almost no oxidation, but towards the last half of the experiment the machine worked much better, and a decided precipitate was formed.

[1] Wright: Am. J. Sci., [3], 4, 26 (1872).

Experiment 4.—Same as above. Temperature, 28o°. With 1.25 liters of carbon monoxide and 3.5 liters of oxygen passing in about two hours, there were only traces of oxidation. The ozonizer was surrounded by ice.

Experiment 5.—One and a half liters of carbon monoxide and 6 liters of oxygen. The monoxide was not dried in this case, but was allowed to bubble through water just before mixing with the ozone. The ozonizer was surrounded by ice. Temperature, 28o°. A slight precipitate soon formed, but did not perceptibly increase during the rest of the time.

Experiment 6.—The amount of ozone formed was determined by passing the gas into solutions of potassium iodide acidulated with dilute sulphuric acid, contained in bottles I and L. The solution was then titrated with a solution of sodium thiosulphate of known strength. The results are necessarily inexact, owing to the impossibility of accurately measuring the oxygen in a gas-holder.

Volume of oxygen, 5.5 liters. The iodine set free required 2.12 cc. of a solution of thiosulphate of such strength that 1 cc. was equivalent to 0.11506 gram iodine. Iodine found, 0.2439 gram, equivalent to 0.02938 gram ozone, or 0.37 per cent. In this experiment and the next a bottle containing an amount of acidulated potassium iodide solution equal to that used in I and L was allowed to stand beside these bottles. A certain amount of iodine was set free. The correction to be applied to I and L was determined by titrating with thiosulphate. During this experiment the machine did not work very well.

Experiment 7.—Everything arranged as in 6. Volume of oxygen, 4 liters. Two dishes containing strong sulphuric acid were placed in the case with the Holtz machine to dry the air, so that it worked up to its maximum efficiency. The iodine set free was 0.2877 gram, equivalent to 0.05444 gram ozone, or 0.95 per cent.

These figures do not agree very closely with those of Jones, but they go to show that the increased oxidation in dry weather is due to the greater amount of ozone formed. We

think it may be fairly concluded that, although ozone does not act on carbon monoxide as readily as we should expect from its apparent unsaturation, still it does cause some oxidation to carbon dioxide, depending on the amount of ozone present in the oxygen. And, further, the oxidation does not take place to an appreciable extent at the ordinary temperature.

JOHNS HOPKINS UNIVERSITY,
May, 1903.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN NITRO DERIVATIVES OF THE VICINAL TRIBROMBENZOL.

BY C. LORING JACKSON AND A. H. FISKE.

The experiments described in this paper form a continuation of the work carried on for several years in this laboratory upon the behavior of benzol derivatives containing nitro groups and halogens. The 1-nitro-3,4,5-tribrombenzol, melting-point 112°, which was the first substance studied, was discovered by Körner,[1] and is easily prepared by treating paranitraniline with bromine and replacing with bromine the amino group in the dibromnitraniline thus obtained.

When treated with a dilute solution of sodic methylate, this 3,4,5-tribromnitrobenzol is converted into the dibromnitroanisol, melting at 122°, prepared by Körner[2] from the silver salt of the 2,6-dibrom-4-nitrophenol and methyl iodide. It follows from this that the atom of bromine in the para position to the nitro group has been replaced by the methoxyl group. This is what would be expected, as owing to its para position this atom is more exposed to the loosening effect of the nitro group than the other two atoms of bromine, which stand in the meta position to it. Staedel,[3] who prepared the substance according to Körner's method, gives the melting-point as 126° to 127°, evidently by an error of the press, as he says that the melting-point observed by him agrees with that of Körner, and gives the correct melting-point 122°.6 in the summary at the end of his paper.

[1] Gazz. chim. ital., 4, 420 (1874).
[2] *Ibid.*, 4, 390 (1876). Körner gives the melting-point 122°.6.
[3] Ann. Chem. (Liebig), 217, 70 (1883).

By reduction with tin and hydrochloric acid this dibromnitroanisol was converted into the 2,6-dibrom-4-aminoanisol, which melts at 64° to 65°. Staedel obtained this substance in the same way, but gives no melting-point for it.

When the 3,4,5-tribromnitrobenzol was treated with a strong solution of sodic methylate it was converted into 4-methoxy-3,5-dibromazoxybenzol,

$$(CH_3O.C_6H_2Br_2)_2N_2O,$$

which melts at 214°. The easy formation of the azoxy compound in this case may be due to the fact that the two places ortho to the nitro group are occupied by hydrogen. In the other bromnitrobenzols studied in this laboratory the positions ortho to the nitro group were occupied by other radicals, and no formation of an azoxy compound has been observed, but many more experiments will be necessary before it can be determined whether this suggestion is entitled to consideration.

Sodic ethylate gave results similar to those obtained with the methylate. A strong solution of sodic ethylate formed the 4-ethoxy-3,5-dibromazoxybenzol, $(C_2H_5O.C_6H_2Br_2)_2N_2O$, which melts at 163°, and was obtained with more ease than the methyl compound. A weak solution of sodic ethylate converted the 3,4,5-tribromnitrobenzol into the 2,6-dibrom-4-nitrophenetol, $C_6H_2Br_2.NO_2.OC_2H_5$, which we found melts at 58° to 59°. Staedel,[1] on the other hand, assigns a melting-point of 108° to this substance. Accordingly, after we had settled the composition of our body by analysis, we determined its constitution by saponifying it, when we obtained a phenol, $C_6H_2Br_2.NO_2.OH$, which showed the melting-point 141° characteristic of the 2,6-dibrom-4-nitrophenol. Finally, in the hope of finding the cause of this difference between Staedel's result and ours, we prepared the dibromnitrophenetol according to Staedel's method, which consisted in making the dibromnitrophenol by treating paranitrophenol with bromine, and heating its silver salt with ethyl iodide; the 2,6-dibrom-4-nitrophenetol thus obtained melted at 58° to 59°, the melting-point of our sample prepared from the tribromnitrobenzol, and not at 108°, the temperature given by Staedel.

[1] Ann. Chem. (Liebig), **217**, 67 (1883).

We are forced to the conclusion, therefore, that Staedel's melting-point, 108°, is incorrect.

By reduction with tin and hydrochloric acid our phenetol yielded the 2,6-dibrom-4-aminophenetol, $C_6H_2Br_2.NH_2.OC_2H_5$, which melted at 107°. Staedel gives the melting-point of this substance as 67°, so that the phenetol with the incorrect melting-point, 108°, gives a phenetidine also with an incorrect melting-point (67° instead of 107°). We can find no explanation for these differences between Staedel's melting-points and ours.

The dibromnitrophenetol was converted into the 4-ethoxy-3,5-dibromazoxybenzol already mentioned, when it was boiled with a strong alcoholic solution of sodic ethylate.

When the 3,4,5-tribromnitrobenzol was boiled for some time with an aqueous solution of sodic hydrate, the 2,6-dibrom-4-nitrophenol was formed. Alcoholic ammonia converted the tribromnitrobenzol into 2,6-dibrom-4-nitraniline, as was proved by Körner.[1] With aniline, even at its boiling-point, the 3,4,5-tribromnitrobenzol seemed to enter into no reaction, as it was recovered afterward unchanged. Sodic acetoacetic ester also had no apparent action on it. Sodic malonic ester formed with it a red salt, which was not studied.

When boiled with a mixture of fuming nitric acid and strong sulphuric acid, the 3,4,5-tribromnitrobenzol was converted into a dinitro compound, $C_6HBr_3(NO_2)_2$, which must have the structure $Br_3$3,4,5.$(NO_2)_2$1,2. It melts at 160° and is much more reactive than the mononitro compound. With sodic methylate, in the cold, it gave a tribromnitroanisol, $C_6HBr_3.NO_2.OCH_3$, by the replacement of a nitro group by a methoxy group. This melts at 109° to 110°. If a boiling solution of sodic methylate in methyl alcoholic acted on the tribromdinitrobenzol, a dibromnitrodimethoxybenzol, $C_6HBr_2.NO_2.(OCH_3)_2$, melting at 81°, was formed by the replacement of an atom of bromine and a nitro group by methoxy groups. When the tribromdinitrobenzol was treated with an alcoholic solution of sodic ethylate in the cold, the tribromnitrophenetol, $C_6HBr_3.NO_2.OC_2H_5$, melting at 74°, was formed. The experi-

[1] Gazz. chim. ital., **4**, 421 (1874).

ment with a boiling solution of sodic ethylate led only to tarry products.

On boiling the 3,4,5-tribrom-1,2-dinitrobenzol with a 10 per cent solution of sodic hydrate a phenol, $C_6HBr_3.NO_2.OH$, was formed, which melted at 120° to 121°. As this gave the anisol, melting at 109° to 110°, when its silver salt was treated with methyl iodide, it must have the same structure as anisol.

Alcoholic ammonia in the cold replaced a nitro group by an amino group, forming a tribromnitraniline, $C_6HBr_3.NO_2.NH_2$, melting at 161°. If the two materials were heated to 100°, a diamino compound, $C_6HBr_3.NO_2(NH_2)_2$, melting at 189° to 190°, was obtained. Neither of these substances gave salts, even when their solutions in benzol were treated with gaseous hydrochloric acid. Boiling aniline produced a substitution of the nitro group by the anilino radical, giving

$$C_6HBr_3.NO_2.C_6H_5NH,$$

melting at 138° to 139°.

The 3,4,5-tribrom-1,2-dinitrobenzol upon reduction with tin and hydrochloric acid, gave the 3,4,5-tribromorthophenylenediamine, $C_6HBr_3(NH_2)_2$, melting at 91°, which formed a salt with 1 molecule of hydrochloric acid, $C_6HBr_3.NH_2.NH_3Cl$. With phenanthrenequinone it gave 3,4,5-tribromdiphenylenequinoxaline (or 3,4,5-tribromphenanthrophenazine),

$$C_6HBr_3N_2C_2C_{12}H_8,$$

which did not melt below 300°. With benzil it gave 3,4,5-tribromdiphenylquinoxaline, $C_6HBr_3N_2C_2C_{12}H_{10}$, a brick-red powder.

Of these derivatives of the 3,4,5-tribrom-1,2-dinitrobenzol the constitution of the tribromnitraniline is established, since there are only two formulas which it is possible to assign to it—$NH_2$1, $Br_2$2,3,4, $NO_2$6 and $NH_2$1.$Br_3$3,4,5.$NO_2$2—and a substance having the second of these was made by Gallivan and one of us[1] by introducing a nitro group into the 3,4,5-tribrom aniline. As this substance melts at 130°, and ours at 161°, it follows that the first of these structures belongs to our compound, which is therefore the 2,3,4-tribrom-6-nitraniline. An

[1] This JOURNAL, **30**, 184 (1898).

attempt to connect the tribromnitrophenol and its ethers with this tribromnitraniline by means of the diazo reaction gave a phenol closely resembling that made directly from the tribromdinitrobenzol, but owing to a mistake in the work the identity of the two substances was not established with certainty. Unfortunately, this mistake was not discovered until it was too late to correct it. We cannot, therefore, present an experimental proof that the nitro group replaced by the hydroxyl is the same as that replaced by the amino group, but we are of the opinion that the following considerations leave little doubt that this is the case. In the 3,4,5-tribrom-1,2-dinitrobenzol, both nitro groups are exposed to the loosening effects of a nitro group in the ortho and an atom of bromine in the para position, but, while the nitro group 1 is but little effected by the third atom of bromine in the meta position, the nitro group 2 is exposed to the marked loosening effect of an atom of bromine in the ortho position, and, therefore, should be the one replaced in all these reactions.

If this reasoning is admitted, these substances receive the following names: 2,3,4-tribrom-6-nitroanisol, melting-point 109° to 110°; 2,3,4-tribrom-6-nitrophenetol, melting-point 74°; 2,3,4-tribrom-6-nitrophenol, melting-point 120° to 121°; 2,3,4-tribrom-6-nitrodiphenylamine, melting-point 138° to 139°.

The nitro group replaced by the methoxy radical in forming $C_6HBr_2.NO_2(OCH_3)_2$ must be that standing at 2 in the 3,4,5-tribrom-1,2-dinitrobenzol, as this substance can be made by treating the tribromnitroanisol with boiling sodic methylate solution. It follows then, without much doubt, that the atom of bromine substituted is that standing at 4, since the other two atoms of bromine stand in the meta position to the nitro group, when the dimethoxy body is made from the anisol. It should be called, therefore, 2,4-dibrom-6-nitroresorcine dimethyl ether, melting-point 81°.

A similar course of reasoning would show that the constitution of the diamino body is 2,4-dibrom-6-nitrometaphenylenediamine, and this result is confirmed by our observation that it did not give the characteristic quinoxaline test for an

orthodiamine, or the Lauth violet test for a paradiamine. It may be objected that these tests might not act with a body containing so many negative groups, but we cannot think this objection of much weight in view of the facts that a quinoxaline was formed easily from 3,4,5-tribromorthophenylenediamine, as described in this paper, and that the 1,4-dibrom-2,5-phenylenediamine gave the Lauth violet test without difficulty.[1]

The most striking observation made in the work with the tribromdinitrobenzol is that the nitro group is replaced more easily than the atom of bromine—certainly an unexpected result—in fact the reactions already described, which take place in the cold, are almost exclusively confined to the substitution of the nitro group, but this cannot be accepted as a general rule, since sodic malonic ester in the cold gave a substance with the formula $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$, to judge from a single determination of bromine, and was, therefore, made by the replacement of an atom of bromine by the malonic ester radical.

EXPERIMENTAL PART.

Preparation of 3,4,5-Tribromnitrobenzol.

Paranitraniline was converted into the dibromparanitraniline by the method of Körner.[2] For this purpose 15 grams of the paranitraniline were dissolved in rather more than 50 grams of ordinary strong hydrochloric acid, and the solution diluted to 2 liters. A stream of air loaded with bromine vapor was then passed through this solution until a permanent red color was imparted to it. The precipitate, after washing, was nearly pure dibromnitraniline, as it melted at 200° to 201° instead of 202°.5. Yield, from 80 to 90 per cent of the theoretical.

The amino group in the dibromnitraniline was next replaced by bromine as follows: Twenty grams of the dibromnitraniline (melting-point 202°) were mixed with 70 cc. of hydrobromic acid (sp. gr. 1.35, b. p. 124° to 126°) and the

[1] This JOURNAL, **28**, 461.

[2] Gazz. chim. ital., **4**, 346 (1874).

thin paste thus formed was treated with sodic nitrite in a 500 cc. flask, which was loosely corked, care being taken by shaking the flask occasionally to expose as large a surface of the mixture as possible to the action of the nitrous fumes. Pieces of the sodic nitrite were added from time to time so as to keep the flask constantly filled with red fumes, and the operation was carried on until the color of the paste had changed from yellow to red, which commonly took place at the end of three or four days. A quantity of hydrobromic acid was then added and the mixture boiled until it ceased to give off red fumes. This treatment converted the red solid into a dark-brown oil, which was separated from the hydrobromic acid, and, after it had hardened, washed and dried at ordinary temperatures. To purify the crude tribromnitrobenzol thus obtained it was dissolved in benzol and the solution boiled with bone-black for half an hour in a flask with a return-condenser, after which it was filtered, allowed to cool, and any yellow solid which separated removed by a second filtration. The filtrate was freed from benzol as completely as possible by distillation on the steam-bath, and the residue stirred while it was cooling so as to get small crystals. These were filtered from the mother-liquor, washed with a small quantity of cold alcohol, and recrystallized from hot alcohol until they melted at 112°. The yield averaged nearly 80 per cent of the theoretical.

Action of Sodic Methylate in the Cold on 3,4,5-Tribromnitrobenzol.

2,6-Dibrom-4-nitroanisol, $C_6H_2Br_2.NO_2.OCH_3$.—Five grams of the 3,4,5-tribromnitrobenzol were mixed with the solution of sodic methylate in methyl alcohol, formed by acting on 0.8 gram of sodium with 25 cc. of methyl alcohol, that is, a little more than 2 molecules of the methylate to each molecule of the tribromnitrobenzol. The mixture was allowed to stand two days in a corked flask, when it was found that the liquid had turned yellow, and deposited crystals. The yellow mother-liquor, on dilution with water, gave a white precipitate, which was filtered out and added to the crystals. In the aqueous

filtrate a strong test for a bromide was obtained, but none for a nitrite. The organic product of the reaction was purified by recrystallizing it from hot methyl alcohol until it showed the constant melting-point 122°, which indicated that it was the dibromnitroanisol, $OCH_3.1.Br_2.2,6.NO_2.4$, melting at 122°.6, that was made by Körner[1] from the silver salt of the 2,6-dibrom-4-nitrophenol and methyl iodide. This result was confirmed by saponifying our substance with sulphuric acid, when it yielded this 2,6-dibrom-4-nitrophenol, as shown by the melting-point 141°.

4-Methoxy-3,5-dibromazoxybenzol.—This substance was obtained when the 3,4-tribromnitrobenzol was treated with a much stronger solution of sodic methylate than that used in making the dibromnitroanisol. Four grams of the tribromnitrobenzol were mixed with the sodic methylate made from 2.4 grams of sodium and 20 cc. of methyl alcohol,[2] that is, over 9 molecules of the methylate to each molecule of the tribromnitrobenzol. The mixture was boiled in a flask with a return-condenser for six hours, after which the product consisted of a solid suspended in a dark-red liquid. The solid was filtered out, washed repeatedly with water, and then with boiling alcohol to remove any 2,6-dibrom-4-nitroanisol which had been formed, and the residue recrystallized from hot benzol till it showed the constant melting-point 214°. Another excellent method of purifying the substance consisted in dissolving it in chloroform and then precipitating out the solid with an excess of alcohol. The compound was dried at 100° and analyzed with the following results:

I. 0.2034 gram substance gave 0.2156 gram CO_2 and 0.0382 gram H_2O.

II. 0.3305 gram substance gave 0.3470 gram CO_2 and 0.0668 gram H_2O.

III. 0.2433 gram gave, by the Carius method, 0.3200 gram AgBr.

IV. 0.2065 gram substance gave 0.2714 gram AgBr.

[1] Gazz. chim. ital., 4, 390 (1874).

[2] Good results were also obtained with 3 grams of sodium and 40 cc. of methyl alcohol.

V. 0.2014 gram substance gave, by the method of Zeisel, 0.1550 gram AgI.

	Calculated for $[C_6H_2Br_2.OCH_3]_2N_2O$.	Found. I.	II.	III.	IV.	V.
C	29.27	28.92	28.64	....	....	....
H	1.74	2.09	2.25	....	....	....
Br	55.75	....	....	55.98	55.93	....
CH_3O	10.80	....	....	....	....	10.15

The substance is, therefore, the 4-methoxy-3-5-dibromazoxybenzol. The formation of this substance depended on the strength of the sodic methylate solution used and not on the fact that the mixture was boiled, as a mixture of the tribromnitrobenzol, even after boiling for two days with a more dilute solution of sodic methylate, gave only the dibromnitroanisol, melting at 122°, with some of the corresponding phenol melting at 141°. On the other hand, the azoxy compound was formed when the mixture of the tribromnitrobenzol and the stronger solution of sodic methylate was allowed to stand in the cold. In every case some of the dibromnitroanisol was formed also, which was obtained from the filtrate and the alcoholic washings. The filtrate also gave a test for a bromide but none for a nitrite.

The methoxydibromazoxybenzol was also made from the dibromnitroanisol, melting at 122°, by boiling a mixture of 3 grams of the anisol and the sodic methylate from 2.25 grams of sodium and 30 cc. of methyl alcohol. After the mixture had been boiled for three hours in a flask with a return-condenser, it was precipitated with water and the precipitate boiled with alcohol to remove any unaltered anisol, when the residue, insoluble in alcohol, showed the melting-point of the azoxy compound, 214°.

Properties of the 4-Methoxy-3,5-bromdiazoxybenzol, $(C_6H_2Br_2.OCH_3)_2N_2O$.—It crystallizes from benzol in radiating, brush-like bundles of yellowish-white needles. It melts at 214° and is easily soluble in chloroform; soluble in benzol; slightly soluble in acetone or glacial acetic acid; nearly insoluble in methyl alcohol or ether; essentially insoluble in alcohol, ligroin, or water, whether hot or cold. It is insolu-

ble in strong hydrochloric acid. A specimen of the substance was found to be unchanged after it had been boiled for four days with a solution of stannous chloride, strong hydrochloric acid, and tin. Aluminium and sodic hydrate also seemed to have no action on it. On the other hand, zinc dust and acetic acid seemed to reduce it, although we did not succeed in isolating the product, and with hydriodic acid it underwent a decomposition reaching apparently to the destruction of the benzol rings.

Reduction of the 2,6-Dibrom-4-nitroanisol (*2,6-Dibrom-4-aminoanisol*).—One gram of the dibromnitroanisol was mixed with about 10 cc. of a solution of stannous chloride prepared from 2 grams of tin, a little granulated tin, and 10 cc. of strong hydrochloric acid, and the mixture was boiled for six hours in a flask with a return-condenser. At the end of this time all the organic matter had gone into solution, and on cooling, a double tin salt in large white flakes crystallized out so freely that the mixture became almost solid. These crystals were filtered out, washed with very little cold water, dissolved in a few cc. of hot water, and the boiling solution treated with an excess of sodic hydrate. A white precipitate was formed in this way, which melted partially in the boiling water. This was filtered out, washed, and after drying for a few minutes boiled out with ligroin (boiling between 70° and 90°), the ligroin extract was filtered hot, and on cooling deposited white crystals of the anisidine, which were recrystallized from ligroin until they showed the constant melting-point 64° to 65°. An additional amount of the substance was obtained by extracting the sodic hydrate solution with ligroin. It was dried *in vacuo* and analyzed with the following result:

0.1251 gram substance gave, by the Carius method, 0.1679 gram of argentic bromide.

	Calculated for $C_6H_2Br_2.NH_2.OCH_3$.	Found.
Br	56.94	57.14

This dibromanisidine has been prepared by Staedel,[1] but he did not give its melting-point, or a full description of its

[1] Ann. Chem. (Liebig), **217**, 71 (1883).

properties, which we have observed as follows: It crystallizes from cold alcohol in rather short, white prisms, sometimes terminated by a basal plane, more often by several planes at a very obtuse angle to each other. It melts at 64° to 65°, and is easily soluble in ethyl or methyl alcohol, ether, benzol, chloroform, acetone, or carbonic disulphide; soluble in glacial acetic acid; slightly soluble in cold ligroin, freely soluble in hot ligroin; insoluble in water. The best solvent for it is ligroin.

For further identification we prepared and analyzed the chloride. For this purpose 0.3 gram of the anisidine, dissolved in 100 cc. of dry benzol, was treated with hydrochloric acid gas. The white precipitate thus obtained was washed with dry benzol, dried *in vacuo*, and analyzed with the following result:

0.2120 gram substance gave, by the Carius method, 0.3446 gram of the mixture of AgCl and AgBr.

	Calculated for $C_6H_2Br_3.OCH_3NH_3Cl$.	Found.
Cl + Br	61.57	61.18

Staedel prepared this chloride, and also the sulphate and oxalate of this dibromanisidine.

Action of Sodic Ethylate on 3,4,5-Tribromnitrobenzol.

2,6-Dibrom-4-nitrophenetol, $C_6H_2Br_2.OCrH_5.NO_2$.–Two grams of the 3,4,5-tribromnitrobenzol dissolved in 5 cc. of benzol were mixed with a solution of sodic ethylate made from 0.5 gram of sodium and 30 cc. of absolute alcohol, and the mixture was allowed to stand at ordinary temperatures for four or more days, after which the brown solution was diluted with a quantity of water and the precipitate washed and purified by crystallization from alcohol, with the aid of bone-black, until it showed the constant melting-point 58° to 59°, when it was dried *in vacuo* and analyzed with the following result:

I. 0.1230 gram substance gave, on combustion, 0.1322 gram CO_2 and 0.0348 gram H_2O.

II. 0.3036 gram substance gave, by the Carius method, 0.3491 gram AgBr.

	Calculated for $C_6H_2Br_3.OC_2H_5NO_2$.	Found. I.	II.
C	29.54	29.32	....
H	2.15	3.16	....
Br	49.23	....	48.93

The yield was essentially quantitative.

Properties of the 2,6-Dibrom-4-nitrophenetol.—It crystallizes from alcohol in long, tapering, very sharp, white needles arranged in radiating groups, and showing a tendency to branch. It melts at 58° to 59°, and is very soluble in ether, benzol, chloroform, or acetone; fairly soluble in hot, less soluble in cold ethyl alcohol; somewhat more soluble in methyl than in ethyl alcohol; soluble in ligroin; essentially insoluble in water. Alcohol is the best solvent for it.

Staedel[1] has prepared a 2,6-dibrom-4-nitrophenetol, which he found melted at 108°. Our compound, which should have the same structure, melts at 58° to 59°. Our analyses leave no doubt that it is a dibromnitrophenetol, but, as it is possible to form two different dibromnitrophenetols from the 3,4,5-tribromnitrobenzol ($OC_2H_5$1.$Br_2$2,6.$NO_2$4 and $OC_2H_5$1.$Br_2$2,3.$NO_2$5), we determined the constitution of our substance as follows: A quantity of the dibromnitrophenetol was saponified by boiling it in a flask with a return-condenser with sulphuric acid of sp. gr. 1.44. The phenol thus obtained, after recrystallization from benzol, melted at 141°, the melting-point of the 2,6-dibrom-4-nitrophenol. There can be no doubt, therefore, that our compound is the 2,6-dibrom-4-nitrophenetol. This 2,6-dibrom-4-nitrophenol was the substance from which Staedel prepared his phenetol, melting at 108°, and accordingly we repeated Staedel's work to see if we could find the reason for the difference between the melting-points observed by him and by us. For this purpose we made the 2,6-dibrom-4-nitrophenol by the action of bromine vapor upon the 4-nitrophenol dissolved in a large quantity of water. The product, which showed the correct melting-point 141°, was converted into the potassium salt with potassic carbonate, and a solution of this precipitated with argentic nitrate to form the silver salt. The dried silver salt was heated to 100° for

[1] Ann. Chem. (Liebig), **217**, 67 (1883).

eight hours in a sealed tube with ethyl iodide. The product, mixed with some alcohol, was poured off from the argentic iodide, and on evaporation yielded crystals of the 2,6-dibrom-4-nitrophenetol, which melted at 58° to 59°, like that prepared by us from 3,4,5-tribromnitrobenzol. As in this experiment we had followed the method of Staedel as carefully as possible, we are forced to the conclusion that he is in error in ascribing the melting-point 108° to the 2,6-dibrom-4-nitrophenetol.

4-Ethoxy-3,5-dibromazoxybenzol, $(C_6H_2Br_2.OC_2H_5)_2N_2O$. — This substance was obtained when the 3,4,5-tribromnitrobenzol was treated with a much stronger solution of sodic ethylate than that which yielded the phenetol. Heating the mixture promotes the formation of the azoxy compound, but, as the product in this case is very impure, it is wiser to carry on the preparation in the cold. Occasionally this compound was formed even with the dilute solutions of the ethylate, which usually gave the phenetol. We have not succeeded in discovering the cause of this abnormal behavior. The best method for preparing this substance was as follows: Ten grams of 3,4,5-tribromnitrobenzol were mixed with the sodic ethylate made from 3.5 grams of sodium and 60 cc. of absolute alcohol, and the mixture allowed to stand in a corked flask at ordinary temperatures for three or more days. The dark-brown liquid thus obtained was diluted with water, and the precipitate, after washing with water, was extracted with a small amount of alcohol to remove any phenetol which might have been formed. The residue was then extracted several times with ligroin, which dissolved the azoxy body, thus separating it from the dark-colored, tarry impurities. It was purified by crystallization from ligroin or benzol until it showed the constant melting-point 163°, when it was dried at 100° and analyzed with the following results:

I. 0.1983 gram substance gave, on combustion, 0.2262 gram CO_2 and 0.0569 gram H_2O.

II. 0.1974 gram substance gave, by the Carius method, 0.2467 gram AgBr.

III. 0.2569 gram substance gave, by the Carius method, 0.3202 gram AgBr.

	Calculated for $(C_6H_2Br_2OC_2H_5)_2N_2O$.	Found. I.	II.	III.
C	31.89	31.91	....	....
H	2.32	3.27	....	....
Br	53.15	....	53.22	53.07

The dibromethoxyazoxybenzol can also be prepared from the dibromnitrophenetol melting at 58° to 59° by boiling it for half an hour with a strong solution of sodic ethylate (0.25 gram of sodium and 30 cc. of alcohol to 1 gram of the phenetol).

Properties of the 3,5-Dibrom-4-ethoxyazoxybenzol.—It crystallizes from benzol in long, very slender, yellowish-white needles, which melt at 163°. It is soluble in benzol or chloroform; slightly soluble in alcohol, methyl alcohol, ether, glacial acetic acid, or ligroin. The best solvent for it is benzol. Sodic hydrate in aqueous solution decomposes it only to a slight extent, even when boiled with it for some time. It forms no salt with hydrochloric acid, which is without action on it even when boiling.

Reduction of the 2,6-Dibrom-4-nitrophenetol (2,6-Dibrom-4-aminophenetol), $C_6H_2Br_2.OC_2H_5.NH_2$.—Three grams of the 2,6-dibrom-4-nitrophenetol were mixed with 15 cc. of the solution of stannous chloride made from 3 grams of tin. Some pieces of tin and a little strong hydrochloric acid were added, and the mixture boiled in a flask with a return-condenser until almost the whole of the phenetol had gone into solution. The solution was filtered hot to get rid of the tin, and the filtrate, on cooling, became filled with white crystals, probably of a double tin salt. These were filtered out and boiled with water and a little sodic hydrate for a few minutes, and the precipitate filtered off after it had solidified on cooling. The filtrate from the crystals treated in the same way gave an additional quantity of the base. The sodic hydrate filtrates, on extraction with ether, gave so little of the base that this treatment is not worth while. The two precipitates were extracted repeatedly with ligroin to separate the organic matter

from hydrate of tin, and the extract purified by crystallization from ligroin until it showed the constant melting-point 107°, when it was dried *in vacuo* and analyzed with the following result:

0.1338 gram substance gave, by the Carius method, 0.1710 gram AgBr.

	Calculated for $C_6H_2Br_2.OC_2H_5.NH_3$.	Found.
Br	54.24	54.38

Properties of the 2,6-Dibrom-4-aminophenetol.—It crystallizes from alcohol in broad, white plates terminated by two planes at an acute angle to each other, with the angle truncated by a basal plane. It melts at 107°. It is freely soluble in benzol, ether, or acetone; soluble in alcohol or chloroform; nearly insoluble in cold, soluble in hot ligroin. Alcohol is the best solvent for it.

The chloride of the base was prepared by passing hydrochloric acid gas into its solution in benzol. The precipitate was washed with benzol, dried *in vacuo*, and analyzed with the following result:

0.2056 gram substance gave, by the Carius method, 0.3175 gram mixture of AgCl and AgBr.

	Calculated for $C_6H_2Br_2.OC_2H_5.NH_3Cl$.	Found.
Cl + Br	58.98	58.11

Staedel,[1] who discovered this dibromphenetidine, gives its melting-point as 67°, whereas we observed it as 107°. The analyses and methods of preparation establish the identity of these two bodies beyond a doubt. We are no more able to explain the difference between the melting-points observed by Staedel and by us than in the corresponding case of the dibromnitrophenetol from which the dibromphenetidine was prepared, where Staedel gives the melting-point 108°, but we found 58° to 59°.

Upon boiling the 3,4,5-tribromnitrobenzol with water containing a little potassic carbonate for sixteen hours very little action was observed. The amount of phenol formed was too

[1] Ann. Chem. (Liebig), 217, 72.

small for identification, and most of the original substance was recovered unaltered. When the 3,4,5-tribromnitrobenzol was boiled with sodic hydrate, on the other hand (1 gram tribromnitrobenzol, 1 gram of sodic hydrate, and 10 cc. of water), for sixteen or more hours, a considerable quantity of the 2,6-dibrom-4-nitrophenol was formed, which was recognized by its melting-point, 141°. Sodic malonic ester seems to react with the 3,4,5-tribromnitrobenzol, as a red substance was formed, but, even after long standing or boiling with a return-condenser, most of the original substance was recovered unaltered. The same remark applies with even greater force to the action of sodic acetoacetic ester. Aniline also, even at its boiling-point, showed little or no action on the 3,4,5-tribromnitrobenzol, which was recovered from the mixture with unaltered melting-point.

3,4,5-Tribrom-1,2-dinitrobenzol, $C_6HBr_3(NO_2)_2$.

To prepare this substance 50 grams of the 3,4,5-tribromnitrobenzol were mixed with 200 cc. of fuming nitric acid and 50 cc. of strong sulphuric acid, and the mixture heated, in a flask closed with a porcelain crucible, to a temperature just below its boiling-point for two hours. At the end of this time a considerable quantity of solid had separated, but, disregarding this, the heating was continued for half an hour longer, and then the product was poured into a large quantity of cold water, and allowed to stand over night. The precipitate was filtered out, and proved pure enough for use in other preparations. The yield was essentially quantitative. For analysis, it was purified by crystallization from alcohol until it showed the constant melting-point 160°, when it was analyzed with the following result:

0.1700 gram substance gave, by the Carius method, 0.2372 gram AgBr.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found.
Br	59.26	59.39

Properties of 3,4,5-Tribrom-1,2-dinitrobenzol.—It forms large, well-formed, yellowish-white prisms, terminated by many planes and apparently belonging to the monoclinic system.

It melts at 160°, and is freely soluble in benzol, chloroform, acetone, or glacial acetic acid; soluble in hot ethyl or methyl alcohol, or ether, slightly soluble in these solvents when cold; slightly soluble in hot, even less so in cold ligroin; essentially insoluble in water. An attempt was made to convert it into the trinitro body by treatment with fuming sulphuric and nitric acids, and, although no definite result was obtained, the indications of the experiment were so favorable that this subject will be taken up hereafter in this laboratory.

Action of Cold Sodic Methylate on the 3,4,5-Tribrom-1,2-dinitrobenzol.

2,3,4-Tribrom-6-nitroanisol, $C_6HBr_3.NO_2.OCH_3$.—A dilute solution of sodic methylate was prepared by adding 1 gram of sodium to 200 cc. of methyl alcohol. After this had cooled, 10 grams of the powdered tribromdinitrobenzol were added and the mixture allowed to stand at ordinary temperatures with frequent shaking. In half an hour the liquid became filled with needles, which were filtered out, washed with water, and recrystallized from hot alcohol until they showed the constant melting-point 109° to 110°. The wash-water gave a test for a nitrite but none for a bromide. It also seemed to contain a small quantity of the salt of a phenol, as it was yellow, and gave a trace of a precipitate when acidified. The new organic substance melting at 109° to 110° was dried *in vacuo* and analyzed with the following results:

I. 0.2012 gram substance gave, by the Carius method, 0.2920 gram AgBr.

II. 0.2954 gram substance gave 0.4290 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OCH_3$.	Found. I.	II.
Br	61.38	61.77	61.81

Properties of 2,3,4-Tribrom-6-nitroanisol.—It crystallizes from alcohol in matted spherical masses of very slender, radiating white needles, which melt at 109° to 110°. It is freely soluble in ether, benzol, chloroform, or acetone; slightly soluble in ethyl or methyl alcohol, glacial acetic acid, or ligroin; essentially insoluble in water. We did not succeed in saponifying it by boiling it with sulphuric acid of sp. gr. 1.44.

Action of Boiling Sodic Methylate on 3,4,5-Tribrom-1,2-dinitrobenzol.

Dimethoxydibromnitrobenzol, $C_6HBr_2.NO_2(OCH_3)_2$. — Two grams of the tribromdinitrobenzol were mixed with the solution of sodic methylate made from 0.25 gram of sodium and 25 cc. of methyl alcohol, and the mixture boiled for an hour in a flask with a return-condenser. Upon pouring the product into water a yellow precipitate was obtained which was purified by recrystallization from alcohol. In most cases it was found necessary to start this crystallization by the introduction of a little of the solid. The aqueous liquid gave a test for a nitrite and for a bromide, and also contained the salt of a phenol, to judge from its yellow color and a slight precipitate when acidified, but the amount was too small for identification. The principal product lost its yellow color on recrystallization and melted constant at 81°, when it was dried *in vacuo* and analyzed with the following result:

0.2818 gram substance gave, by the Carius method, 0.3116 gram AgBr.

	Calculated for $C_6HBr_2.NO_2(OCH_3)_2$.	Found.
Br	46.91	47.06

The same substance was formed also by boiling the anisol, $C_6HBr_2.NO_2.OCH_3$, with a methyl alcohol solution of sodic methylate.

Properties of the Dimethoxydibromnitrobenzol.—When crystallized from alcohol, it forms tufts of very slender, long, branching, white needles, which melt at 81°. It shows a tendency to turn brown on standing. It is freely soluble in alcohol, ether, benzol, chloroform, or acetone; slightly soluble in methyl alcohol, glacial acetic acid, or ligroin; essentially insoluble in water. Alcohol or ether is the best solvent for it. Our attempts to saponify this substance with sulphuric acid, or to reduce it with tin and hydrochloric acid, led to unpromising black tars.

Action of Cold Sodic Ethylate on 3,4,5-Tribrom-1,2-dinitrobenzol.

2,3,4-Tribrom-6-nitrophenetol, $C_6HBr_3.NO_2.OC_2H_5$. — Six grams of the 3,4,5-tribrom-1,2-dinitrobenzol were mixed with the sodic ethylate made from 0.8 gram of sodium and 45 cc. of absolute alcohol, and the mixture shaken at ordinary temperatures for about fifteen hours. The product, which was more highly colored than in the corresponding experiment with the methylate, was precipitated with water. The aqueous filtrate gave a strong test for a nitrite, a weaker test for a bromide, and contained a minute amount of some phenol. The precipitate, which was nearly white, was purified by recrystallization from alcohol, until it showed the constant melting-point 74°. The substance was deposited from its alcoholic solution as an oil, which solidified when touched with a crystal of the compound. The pure body was dried *in vacuo* and analyzed with the following results:

0.1988 gram substance gave, by the Carius method, 0.2755 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OC_2H_5$.	Found.
Br	59.40	58.95

Properties of the Tribromnitrophenetol.—It crystallizes from alcohol in little, white rosettes, which turn yellow, and afterward brown, on standing. It melts at 74°. It is freely soluble in ether, benzol, chloroform, or acetone; slightly soluble in alcohol, methyl alcohol, glacial acetic acid, or ligroin. We tried to saponify it by boiling it with sulphuric acid of sp. gr. 1.44, but obtained only dark decomposition-products, from which we did not succeed in isolating a definite compound.

When the action of the sodic ethylate on the 3,4,5-tribrom-1,2-dinitrobenzol was carried on at the boiling-point of alcohol, the product was a reddish tar of most unpromising appearance.

Action of an Aqueous Solution of Sodic Hydrate on 3,4,5-Tribrom-1,2-dinitrobenzol.

Ten grams of the 3,4,5-tribrom-1,2-dinitrobenzol were boiled

in a flask with a return-condenser with 150 cc. of a 10 per cent solution of sodic hydrate prepared from sodium. The liquid turned dark-red almost immediately, and in a few hours began to deposit a bright crimson, crystalline precipitate. To make the reaction as complete as possible the boiling was continued for about fourteen hours, after which the liquid was allowed to cool and the precipitate filtered out. It was then washed through the filter with hot water in order to separate it from unaltered tribromdinitrobenzol. A portion of this filtrate was acidified with dilute nitric acid, the precipitate formed filtered out, and the filtrate tested for a nitrite with starch paste and potassic iodide, when a strong test was obtained. Another portion of the filtrate showed a mere trace of bromide with argentic nitrate. The main portion of the filtrate was acidified with hydrochloric acid, which threw down a yellow crystalline precipitate of the free phenol. The solution was kept cool during the acidification, as otherwise the precipitate showed a tendency to be tarry. The substance was also purified sometimes by precipitating at once with hydrochloric acid and removing the unaltered tribromdinitrobenzol with cold benzol, in which it is soluble, but the phenol nearly insoluble. This separation, however, is rather more tedious than that with boiling water. The crude phenol in either case was recrystallized from hot benzol until it showed the constant melting-point 120° to 121°, when it was dried and analyzed with the following results:

I. 0.2622 gram substance gave, by the Carius method, 0.3939 gram AgBr.

II. 0.2135 gram substance gave 0.3209 gram AgBr.

	Calculated for $C_6HBr_2.NO_2.OH$.	Found. I.	II.
Br	63.83	63.95	63.96

These analyses, in connection with those of its salts given later, show that the substance was formed by the replacement of one nitro group by a hydroxyl. Its constitution is probably $HO1.Br_2 2,3,4.NO_2 6$, and although this has not been proved experimentally, the arguments given in the introduction to this paper are so strongly in favor of this constitution

that we shall call it provisionally the 2,3,4-tribrom-6-nitrophenol.

Properties of the 2,3,4-Tribrom-6-nitrophenol.—It crystallizes from hot benzol in rather thick, yellow prisms with square, or nearly square ends, and melts at 120° to 121°. It is freely soluble in chloroform, or acetone, or in hot benzol, but is nearly insoluble in cold benzol; soluble in alcohol, methyl alcohol, ether, or glacial acetic acid; slightly soluble in water or ligroin. The best solvent for it is hot benzol. Fuming nitric acid seems to destroy it completely. It dissolves easily in an aqueous solution of sodic hydrate with a bright-red color.

Sodium Salt of the 2,3,4-Tribrom-6-nitrophenol, $C_6HBr_3.NO_2.ONa$.—This substance was prepared by treating the pure phenol with sodic hydrate made from sodium and water, and purified by crystallization from hot water. It can also be prepared from the crude sodium salt, which is the direct product of the reaction, by washing it with cold water and then recrystallizing it from boiling water. After standing over night in a desiccator it was dried at 110°, when the loss amounted to less than 0.3 per cent, which showed that it was free from water of crystallization.

0.4018 gram salt yielded 0.0716 gram Na_2SO_4.

	Calculated for $C_6HBr_3.NO_2.ONa$.	Found.
Na	5.78	5.77

The salt forms bright crimson crystals, which are very slightly soluble in cold water, soluble in hot. It is more soluble in alcohol than in water. An aqueous solution of the salt gave a yellowish-orange precipitate with strontic nitrate, a brilliant reddish-orange precipitate with baric nitrate, and a red, flocculent precipitate with plumbic acetate.

Silver Salt of the 2,3,4-Tribrom-6-nitrophenol, $C_6HBr_3.NO_2.OAg$.—This substance was made by adding argentic nitrate to a solution of the sodium salt. The brilliant-red precipitate was washed with hot water and dried *in vacuo*.

0.4431 gram salt gave, when heated in a sealed tube with nitric acid, 0.1707 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OAg$.	Found.
Ag	22.37	22.13

It forms a brilliant red powder, essentially insoluble in cold water, but very slightly soluble in boiling water, from which it separates in small, red needles.

In order to connect this phenol with the anisol formed by the action of sodic methylate on the 3,4,5-tribrom-1,2-dinitrobenzol, we tried, as already stated, to saponify the anisol, and when this led to no satisfactory result we turned our attention to preparing the anisol from the silver salt of the phenol. For this purpose 0.5 gram of the salt was heated to 100° in a sealed tube with 10 cc. of methyl iodide, for six hours. The alcoholic extract of the product deposited crystals which, after purification by recrystallization, melted at 109° and crystallized in the characteristic form of the anisol. There can be no doubt, therefore, that the same nitro group is replaced by the hydroxyl and by the methoxyl group.

Sodic malonic ester acted on the 3,4,5-tribrom-1,2-dinitrobenzol in benzol solution, giving a red salt. On acidifying this a substance was obtained melting at 103° to 104°, which, according to a single determination of bromine, had the formula $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$ (calculated 33.06, found 33.09), but as this is the only case observed by us in which an atom of bromine has been replaced in preference to a nitro group, we do not feel inclined to accept this formula until its correctness has been tested by additional experiments. Sodic acetoacetic ester also gave a similar red salt with the 3,4,5-tribrom-1,2-dinitrobenzol.

Action of Alcoholic Ammonia on 3,4,5-Tribrom-1,2-dinitrobenzol in the Cold.

2,3,4-Tribrom-6-nitraniline, $C_6HBr_3.NO_2.NH_2$.—Ten grams of the tribromdinitrobenzol were mixed with 150 cc. of an alcoholic solution of ammonia in an Erlenmeyer flask, and the mixture shaken for half an hour. A yellow, crystalline precipitate was formed in such quantity as to nearly fill the solution. It was allowed to stand over night to complete the reaction, after which it was poured into water and the yellow

precipitate collected on a filter. The aqueous filtrate gave a strong test for a nitrite and a very faint one for a bromide. The washed precipitate was allowed to dry and then purified by recrystallization from benzol until it showed the constant melting-point 161°, when it was dried *in vacuo* and analyzed with the following result:

0.2486 gram substance gave, by the Carius method, 0.3754 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.NH_2$.	Found.
Br	64.00	64.01

The substance has evidently been formed by the replacement of one nitro group by the amino group. It is an isomer of the tribromnitraniline, prepared, by Gallivan and one of us,[1] by the action of nitric acid on the 3,4,5-tribromacetanilide, since this substance melts at 130°. As this body, from the method of its preparation, must have the constitution $NH_2 1$, $Br_3 3,4,5.NO_2 2$, it follows that our compound melting at 161° must have the only other possible structure, $NH_2 1.Br_3 2,3,4.NO_2 6$. An attempt to convert the 2,3,4-tribrom-6-nitraniline into the corresponding phenol by the diazo reaction gave a product which showed a strong resemblance to the tribromnitrophenol, melting at 120° to 121°, described above. On account of a mistake in the work we cannot bring an absolute proof of the identity of these two bodies, and, unfortunately, this mistake was discovered so late that it could not be corrected without beginning the work from paranitraniline, which it is impossible for us to do at present. The structural formulas assigned to this phenol and its ethers are, therefore, not established by strict proof, although there is little doubt of their correctness.

Properties of the 2,3,4-Tribrom-6-nitraniline.—It crystallizes from benzol in bright-yellow, hair-like needles in radiating bunches, each made up of a few crystals. It melts at 161°. It is freely soluble in benzol, chloroform, or acetone; soluble in ether, methyl alcohol, or glacial acetic acid; slightly soluble in alcohol; and insoluble in cold ligroin or in water. In

[1] This JOURNAL, 20, 184 (1898).

the hope of making a salt, some of the substance was dissolved in anhydrous benzol and treated with gaseous hydrochloric acid. No precipitate was formed, and the solution deposited the unaltered substance recognized by its melting-point, 161°.

A great many attempts were made to convert the substance into the corresponding nitrotetrabrombenzol as a step toward the preparation of the vicinal tetrabrombenzol, but our experiments in this direction led to no decisive results.

Action of Alcoholic Ammonia on 3,4,5-Tribrom-1,2-dinitrobenzol at 100°.

Dibromnitrophenylenediamine, $C_6HBr_2.NO_2(NH_2)_2$. — Two grams of the 3,4,5-tribrom-1,2-dinitrobenzol were heated to 100° in a sealed tube with 10 cc. of alcoholic ammonia for three days. At the end of this time the contents of the tube were washed into a beaker of water, when, upon standing, a yellow precipitate appeared, which was filtered out from the orange liquid. In the filtrate, both nitrite and bromide were found, and also the tribromnitrophenol melting at 120° to 121°. The precipitate was recrystallized from hot alcohol until it showed the constant melting-point 189° to 190°, when it was dried at 100° and analyzed with the following result:

0.0984 gram substance gave, by the Carius method, 0.1187 gram AgBr.

	Calculated for $C_6HBr_2.NO_2(NH_2)_2$.	Found.
Br	51.44	51.36

The substance is formed, therefore, by the replacement of 1 atom of bromine and one nitro group by two amino groups. The nitro group replaced is undoubtedly that lying between one atom of bromine and the second nitro group, as this was the one replaced by the amino group during the action of alcoholic ammonia in the cold. The bromine replaced would then be the atom para to the remaining nitro group, as no other is in a position to be replaced easily, if the tribromnitraniline is formed before the replacement of the bromine. This would give the substance the constitution $Br_2$2,4.$NO_2$6.$(NH_2)_2$1,3. Some qualitative experiments confirmed this

view of the structure of the diamine. A small quantity of it gave no blue color, when treated with hydrochloric acid, ferric chloride, and sulphuretted hydrogen. It would seem, therefore, that it is not a paradiamine. Another sample gave no action with a concentrated acetic acid solution of phenanthrenequinone, even when the mixture was warmed, which would indicate that it was not an orthodiamine. This leaves only the meta position for the two amino groups, which agrees with the conclusion arrived at on the general considerations stated above. We therefore adopt the name 2,4-dibrom-6-nitrometaphenylenediamine for this substance, but it should be remembered that this constitution does not rest on strict experimental proof, as the absence of the reaction for a para- or orthodiamine may have been due to the presence of the strongly negative radicals in the molecule, although this does not seem very probable.

Properties of the 2,4-Dibrom-6-nitrometaphenylenediamine.—It crystallizes in hour-glass-shaped bunches of branching needles, which have a bright-yellow color and melt at 189° to 190°. It is very freely soluble in acetone; soluble in alcohol, methyl alcohol, ether, chloroform, or glacial acetic acid; slightly soluble in benzol; very slightly soluble in ligroin; essentially insoluble in water. The best solvent for it is hot alcohol. It forms no chloride, even when a solution of it in benzol is saturated with gaseous hydrochloric acid.

Action of Aniline on the 3,4,5-Tribrom-1,2-dinitrobenzol.

2,3,4-Tribrom-6-nitrodiphenylamine, $C_6HBr_3.NO_2.NHC_6H_5$.—Half a gram of the 3,4,5-tribrom-1,2-dinitrobenzol was boiled with a few cubic centimeters of aniline, in a test-tube, for about a minute. After it had cooled the solution was poured into water and the excess of aniline removed with dilute hydrochloric acid. The reddish-brown product, after being washed with dilute hydrochloric acid and water, was recrystallized from alcohol until it showed the constant melting-point 138° to 139°, when it was dried and analyzed with the following result:

0.2173 gram substance gave, by the Carius method, 0.2726 gram AgBr.

	Calculated for $C_6HBr_3.NO_3.NHC_6H_5$.	Found.
Br	53.21	53.38

Properties.—When first crystallized from alcohol it gave a mixture of short, bright-red prisms and rosettes of long, delicate, yellow needles, but after several crystallizations from alcohol it was converted entirely into the red prisms. It seems probable from this observation that it occurs in two modifications, as this is not unusual in related aniline bodies.[1] It melts at 138° to 139°. It is soluble in ether, benzol, chloroform, or acetone; slightly soluble in alcohol, methyl alcohol, or glacial acetic acid; insoluble in ligroin or water. The best solvent for it is alcohol.

Reduction of 3,4,5-Tribrom-1,2-dinitrobenzol.

3,4,5-Tribromorthophenylenediamine, $C_6HBr_3(NH_2)_2$.

Twenty grams of the 3,4,5-tribrom-1,2-dinitrobenzol were warmed on the steam-bath in an Erlenmeyer flask with tin and strong hydrochloric acid for a day. The grayish residue was filtered out, boiled with a small quantity of aqueous sodic hydrate to remove hydrates of tin, and this filtered off while nearly boiling. The diamine was then extracted from the insoluble part with acetone, leaving the metallic tin. The residue, after evaporating off the acetone, was purified by crystallization from alcohol and analyzed with the following result:

0.1600 gram substance gave, by the Carius method, 0.2610 gram AgBr.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found.
Br	69.56	69.42

This analysis was confirmed by one of the chloride made by dissolving the diamine in benzol, saturating with gaseous hydrochloric acid, and washing the precipitate with benzol, when it was dried *in vacuo* and analyzed.

[1] This JOURNAL, **14**, 348; **16**, 35; **26**, 5.

0.1686 gram substance gave, by the Carius method, 0.3107 gram AgBr and AgCl.

	Calculated for $C_6HBr_3.NH_2.NH_3Cl$.	Found.
Br + Cl	72.21	71.76

The melting-point observed by us was 91°, but owing to the ease with which the diamine turned brown in the air we do not feel certain that it is exact. It is freely soluble in ether or acetone ; soluble in alcohol, methyl alcohol, benzol, or glacial acetic acid ; slightly soluble in chloroform ; essentially insoluble in ligroin or water. With hydrochloric acid it gives the salt $C_6HBr_3.NH_2.NH_3Cl$, as already mentioned.

Diphenylene-3,4,5-tribromquinoxaline, $C_6HBr_3N_2C_2C_{12}H_8$. — Two grams of the diamine just described, dissolved in about 30 cc. of alcohol, were mixed with 1.2 grams of phenanthrenequinone, dissolved in somewhat more than 125 cc. of glacial acetic acid. The mixture nearly solidified, and after standing half an hour the precipitate was sucked dry on the pump, extracted several times with a mixture of acetone and very little benzol, pressed on a porous plate, and dried in a desiccator containing calcic hydrate and chloride.

0.2368 gram substance gave, by the Carius method, 0.2602 gram AgBr.

	Calculated for $C_6HBr_3N_2C_{14}H_8$.	Found.
Br	46.40	46.77

It formed a yellow solid, which did not melt even at 250°, and was essentially insoluble in all solvents.

Diphenyl-3,4,5-tribromquinoxaline, $C_6HBr_3N_2C_2(C_6H_5)_2$. — Two grams of the orthodiamine dissolved in alcohol were mixed with 1.2 grams of benzil dissolved in glacial acetic acid. At first there was no action, but after adding a few crystals of benzil a brown precipitate began to form, which was deposited in considerable quantity after the mixture had stood over night. It was purified by washing with a small quantity of alcohol and dried in a desiccator over calcic chloride and lime.

0.2153 gram substance gave, by the Carius method, 0.2345 gram AgBr.

	Calculated for $C_6HBr_3.N_3C_2(C_6H_5)_2$.	Found.
Br	46.24	46.34

It forms a light, brick-red powder, freely soluble in benzol or chloroform; soluble in ether or acetone; slightly soluble in alcohol, methyl alcohol, or glacial acetic acid; essentially insoluble in ligroin or water.

OBITUARY.

HENRY BARKER HILL.

The death of Henry Barker Hill, on April 6, 1903, left a gap in the ranks of American chemists which will not be easily filled. Born at Waltham, April 27, 1849, he grew up in a scholarly atmosphere, as he was the son of the Rev. Thomas Hill, president of Antioch College, and later of Harvard University. After graduating from Harvard College, in the class of 1869, he spent a year in Berlin, studying chemistry under A. W. Hofmann, and in 1870 accepted a position in Harvard University, where he served for the following thirty years as Assistant, Assistant Professor, Professor, and Director of the Laboratory.

He took up his duties in Cambridge with only a meagre equipment as a chemist and an enthusiastic determination to make a place for himself in chemical research, but the necessary training came slowly, as he was without a teacher and hampered by the onerous duties of his position, so that his first paper was not published till 1876. This paper, however, showed none of the crudeness and uncertainty of touch usually characteristic of first papers, but seemed rather the work of a mature finished chemist. In it he described methyluric acid, and by following the fate of the methyl group in its decomposition-products succeeded in throwing much light on the constitution of uric acid.

His attention, however, was soon diverted from this line of work, promising as it was, by his discovery of furfurol among the waste products of the manufacture of acetic acid by heating wood at comparatively low temperatures, and the exploration of the almost unknown field thus opened kept him busy till the end of his life. His work on the furfurane group is described in over thirty papers, and among his most strik-

ing achievements may be noted the full study of mucobromic and mucochloric acids with the determination of their puzzling constitution, and the investigation of numerous substituted propionic, acrylic, and propiolic acids derived from them; the description of the brom- and chlorpyromucic acids, in which the interesting fact was brought out that these two halogens differ in their behavior with pyromucic acid; the discovery of nitromalonic aldehyde, and a long line of brilliant aromatic syntheses from it; a study of methylfurfurol, found in the fractions boiling above furfurol, and of its most important derivatives. At the time of his death he was investigating pyrazol compounds from the oxime of nitromalonic aldehyde, and the reduction-products of dehydromucic acid, some of which he had succeeded in separating into the optically active forms.

His work has converted the furfurane group from one of the least known to one of the most perfectly explored domains of chemistry—a monument of which any chemist may feel proud.

An examination of these papers brings out Hill's great qualities as a chemist—his grasp of the subject and power of close and logical reasoning, his uncommon experimental ability, and above all the thoroughness and accuracy which were his most striking and peculiar characteristics. These were the expression of his almost passionate devotion to truth. Most chemists are content to accept the work of their students after testing it in two or three places, but he was never willing to publish until he had repeated the whole of it with his own hands, and if this diminished the number of his papers, it gave them a finish and authority rarely, if ever, found in those of others.

In his teaching the same thoroughness and accuracy were conspicuous. No one ever heard an incorrect statement in his lectures, which were models of comprehensiveness and preservation of the just relation between the important and the unimportant. In his course in investigation the rigorous thoroughness of his work repelled many students, but this did not displease him, as he always preferred quality to quantity.

This is not the place to dwell on his wonderful executive ability, which converted an antiquated building, planned for 40 students, into an adequate laboratory for 700, and organized the varied business of this large department so that it runs smoothly even now, when deprived of its chief. But attention should be called to the new forms of apparatus with which he has enriched the laboratories at Cambridge—the unique hoods and water-baths for the public rooms, and his

many devices for research work, some of which will soon be described in this JOURNAL.

His overflowing energy was not confined to his profession. His reading was wide and judicious in the literatures of more than one language, and he was a genealogist and a musician of no mean attainments.

In this brief note I have tried to show Hill as he was, a man of wide interests and of many and varied excellencies, an admirable teacher, a business man of marked ability, an ingenious inventor, a great chemist, and above all a lover of truth. C. L. J.

REVIEWS.

EINFÜHRUNG IN DIE ELEKTROCHEMIE, NACH DER ELEKTROLYTISCHEN DISSOCIATIONSTHEORIE. Bearbeitet von PETER GERDES. Mit 48 in den Text gedruckten Abbildungen. Druck und Verlag von Wilhelm Knapp. Halle, a. S. 1902. pp. 123.

The ground covered by this little book can be seen from the table of contents. A discussion of electrical units is followed by an account of osmotic pressure, which omits the all-important work of Morse in this field. Chapter III treats of electrolysis and II of polarization. The subject of the neutralization of acids and bases is followed by a brief and fairly satisfactory description of a number of the most common forms of primary cells, including the Daniell, Bunsen, Leclanché, and bichromate batteries. This is followed by a brief account of the electrolytic deposition of the metals.

The book will undoubtedly be found useful by those who have not the time nor inclination to read some larger work on physical chemistry. H. C. J.

ASSAYING AND METALLURGICAL ANALYSIS FOR THE USE OF STUDENTS, CHEMISTS, AND ASSAYERS. By E. L. RHEAD, Lecturer on Metallurgy, Municipal School of Technology, Manchester, and A. HUMBOLDT SEXTON, F.S.C., F.C.S., Professor of Metallurgy, Glasgow, and West of Scotland Technical College. London: Longmans, Green & Co. 1902.

This beautifully printed and illustrated book is written as a comprehensive handbook, to include all the work likely to be required in the laboratory or assay office. It is too large and too varied in contents to supplant the smaller manuals of assaying or of analysis, but it covers the entire field.

Part I., 52 pages, describes laboratory apparatus and general methods. In Part II., 236 pages, under the name of each metal, a complete description of compounds, reactions,

and analytic methods is given. For example, under the heading Bismuth, the ores and alloys are described, as are the chemical reactions by tests in the dry way and in solution; the dry assay, (*a*) of ores free of sulphur, (*b*) of sulphurized ores free of copper, (*c*) of ores with copper present; refining; the wet assay; gravimetric methods, including estimation as oxide, as metal, by precipitation as sulphide; treatment of antimonial and arsenical ores; electrolytic assay; volumetric methods; Abel and Fields' method for the determination of bismuth in copper.

Part III., 108 pages, gives examples of metallurgical analysis. This part also is very satisfactory, and avoids repetition by copious cross-references in the text. As an example taken at random, under the heading Silicon in Iron and Steel, the following methods are well treated: 1. Estimation of silicon by solution of the metal in acid and weighing as silica; 2. Drown's sulphuric acid method; 3. Allen's method; 4. Estimation by iodine; 5. By chlorine.

The book is indeed a comprehensive laboratory handbook, and as such should be welcomed in all laboratories, particularly in those for technical and commercial work. E. R.

GUIDE TO PREPARATION WORK IN INORGANIC CHEMISTRY FOR STUDENTS OF CHEMISTRY AND PHARMACY. By DR. REINHART BLOCHMANN, Professor at the University of Königsberg, with numerous illustrations. Authorized translation by JAMES LEWIS HOWE, Washington and Lee University. Published by the Department of Chemistry, Washington and Lee University, Lexington, Virginia. pp. 65. Price, 60 cents.

The first German edition of Blochmann's book was published in 1895. A review of it appeared in the same year in this JOURNAL,[1] in which it was favorably mentioned.

Few teachers of chemistry pay enough attention to inorganic preparations. No other elementary work interests students so much. If a beginner in the laboratory, who has worked a little ahead of his class, is allowed to fill up extra time by making one or two preparations with due care, the stimulus that "making" something gives him will be felt in his attitude toward his later work.

Professor Blochmann uses inexpensive material and ingeniously utilizes the product or by-product of one preparation as material for others.

Professor Howe has used this book for several years in his own classes, and has made an excellent translation from a copy specially corrected and annotated by the author. It is to be hoped that as this excellent little manual is now obtain-

[1] This JOURNAL, 17, 544.

able in English translation at a low price it may come into frequent use. E. R.

A Course in Qualitative Chemical Analysis. By F. P. Venable, Ph.D., F.C.S., Professor of Chemistry in the University of North Carolina. Revised by Alvin S. Wheeler, A.M., Ph.D., Associate Professor of Chemistry in the University of North Carolina. Fourth edition. New York: University Publishing Co. 1902.

Professor Venable's little book, while very brief and simple, gives careful directions for work and clear explanations of the various reactions. It may be commended to those who prefer a short manual.

The General Principles of Physical Science: An Introduction to the Study of the General Principles of Chemistry. By Arthur A. Noyes, Professor of Theoretical Chemistry in the Massachusetts Institute of Technology. New York: Henry Holt & Co. 1902. pp. 172.

The work in hand is not a complete treatise but simply the introduction to a large work on the general subject of theoretical chemistry. In the author's words: "It forms the first introductory part of a projected work upon this science to be entitled 'The General Principles of Chemistry,' the latter parts of which are to treat in succession of the general theories of chemistry, of the relations between physical properties and chemical composition, of the principles relating to the occurrence and equilibrium of chemical changes, and of the principles relating to the energy changes attending chemical changes."

The introduction deals with the object, the methods, and the subdivisions of science, the fundamental concepts of physical science, the general principles relating to matter, and the general principles relating to energy.

It is obvious that this but paves the way for the general discussion of theoretical or physical chemistry. The style is unusually clear and concise, and the work as a whole will be a valuable contribution to physical chemical literature.

H. C. J.

Lehrbuch der allgemeinen Chemie. Von Dr. Wilhelm Ostwald, Professor an der Universität zu Leipzig. In zwei Bänden. Zweite umgearbeitete Auflage; zweiten Bandes, zweiter Teil; Verwandtschaftslehre, erster Teil, mit 389 Textfiguren. Verlag von Wilhelm Engelmann. 1896–1902. pp. 829–1188.

The conclusion of the second part of the second volume of Ostwald's Lehrbuch will be welcomed by all, and especially by those who possess the earlier portions of this great handbook on physical chemistry. The number in hand treats of the subject of chemical equilibrium of the second order, and

then takes up and completes the discussion of chemical equilibrium of the third order.

The second edition of the "Lehrbuch" is, however, not yet completed. The second part of the second volume is to be followed by a third part, which will treat of solid solutions, isomorphous mixtures, enantiomorphous crystals, electrochemical equilibrium, catalysis, dissociation and equilibrium constants, etc. This will then be followed by a supplement, which will deal systematically with the work which has been published during the appearance of the various parts of the second edition.

With this will end the gigantic task which Ostwald has imposed upon himself, and for which physical chemistry in all time will owe a deep and lasting debt of gratitude.

H. C. J.

LA CIDRERIE MODERNE OU L'ART DE FAIRE LE BON CIDRE. Par GEORGES JACQUEMIN, Directeur scientifique de l'Institut La Claire, et HENRI ALLIOT, Ingénieur agricole. Malzéville-Nancy: Imprimerie Edg. Thomas. 1902. pp. 712. Price, 10 fr.

The authors, who conduct a research laboratory for the study of agricultural chemistry and related subjects, have undertaken to publish a series of monographs under the general title: "La Technologie agricole moderne." The book before us is the first of these. The subject is treated with thoroughness from different points of view. There are chapters on the history of cider, its hygienic effects, and statistics. The structure and composition of apples and pears, the methods of propagating from seed, the different ways of grafting, and the most approved cultural methods of pears and apples are given, as well as an account of their diseases. Then follow chapters on the care of the fruit and machinery, the extraction of the juice, the ferments of cider, the best methods of fermentation and preservation of cider and perry. The diseases of cider and their treatment, the manufacture of alcohol and vinegar, and the preparation of dried apples and pears are also discussed. On the whole, the book will be of value to any one engaged in this business. There are numerous illustrations.

C. E. W.

DIE BESCHÄDIGUNG DER VEGETATION DURCH RAUCH: HANDBUCH ZUR ERKENNUNG UND BEURTEILUNG VON RAUCHSCHÄDEN. By E. HASELHOFF, Director of the Agricultural Experiment Station in Marburg a. d. Lahn, and G. LINDAU, Privatdocent in Botany and Curator of the Royal Botanical Museum in Berlin. Berlin: Gebrüder Borntraeger. 1903. pp. 412. 27 illustrations.

This interesting book is a study of one of the most important and annoying problems with which the forester and agri-

culturist has to deal. It has long been recognized that smoke affects vegetation injuriously, and many observers have investigated the question, both in the field and in the laboratory. This book gives an account of much of this work, in which the authors had a share, and shows, as far as possible, just what part is played by the different constituents of smoke from dwellings, factories, acid works, and metallurgical furnaces. The greatest injury is not caused by the solids (soot, etc.) in the smoke but by the gases, among which sulphur dioxide is the most harmful, especially as it is produced nearly always when fuel is burned. It has been estimated that the various factories in St. Helens, England, send into the air 36,108,000 kilograms of sulphur in the form of sulphur dioxide, etc., each year. Most of this comes from the coal. Besides this, the effects of chlorine, hydrochloric acid, hydrofluoric acid, nitric acid, acetic acid, ammonia, hydrogen sulphide, bromine, asphalt, illuminating gas, pyridine, phenol, flue dust, etc., have been investigated. The specific action of the different poisons and the means of distinguishing between the injuries caused by them and insects, etc., are described as far as possible.

The physiological and structural changes in the leaves, the injury done to vegetables and forest trees, and the relative power of resistance of different species of trees are all studied. The injury caused by a given factory extends over an ellipse with its long axis in the direction of the prevailing wind, and with the factory at one of the foci; that is, the harm done is greatest to leeward. Evergreens, such as pine, spruce, and larch, suffer more than deciduous trees, which practically escape the action of the smoke for a part of the year, during which time they have a chance to recuperate.

The book is of great interest, not only to those for whom it was written, but also to the chemist and botanist.

C. E. W.